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The Linear Thermal Expansion and Alpha-Gamma Transformation Temperature of Pure Iron

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We have recently measured the linear thermal expansion between room temperature and 950°C of ten samples of specially purified iron by means of a vacuum interferometer.[1] The results for two representative samples (sample *A*, carbonyl iron held in hydrogen at 1500°C for 18 hours, and sample *B*, carbonyl iron melted in hydrogen) are given in Table I and Fig. 1. The temperature variation of

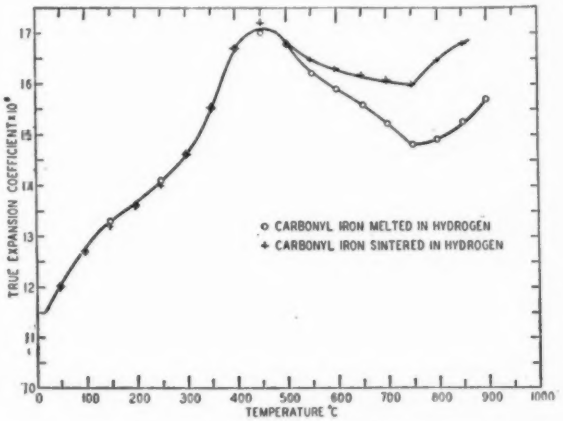

Fig. 1. Thermal expansion coefficient of iron as a function of temperature.

the true expansion coefficient shown is typical of all but two of ten specimens examined; with rising temperature the coefficient increases, passes through a maximum between 400° and 500°, falls to a minimum at, or very near, the Curie point then increases again to the α–γ transformation, that is, to the change from a body-centered to a face-centered lattice. Quantitatively the coefficients for temperatures below 600° are in agreement but at higher temperatures there are differences, too great to be accounted for by experimental error, which indicate that between 600° and 900° the thermal expansion is sensitive to very small differences in composition or to previous treatment or to both.

There is no abrupt change in length at the Curie point, only a point of inflection on the length-temperature curve. No completely satisfactory explanation of the minimum coefficient has been found but calculations by Powell[2] suggest that it is associated with the change in the strength of the binding between atoms which, on Heisenberg's theory of ferromagnetism, accompanies demagnetization.

The temperature of the transformation from body-centered to face-centered structure appears to be very sensitive to the presence of even slight amounts of impurity, varying with the sample from 903° to 940°. Sample *A* transformed at 928±2° on heating and on cooling (rate *ca.* 3.0°/min.), sample *B* at 915±2°. Judging by the behavior in passing through this change in lattice, sample *A* is the purest of all the specimens studied and we believe that 928°, although 20° higher than the value now widely accepted, is close to the true transformation temperature of

[1] Austin, Physics **3**, 240 (1932).

[2] Powell, Proc. Phys. Soc. London **42**, 390 (1930).

TABLE I. *True linear expansion coefficient* $\alpha_t[=(1/l_0)(dl/dt)]$.

Sample	100°	200°	300°	400°	500°	600°	700°	800°
A. Powdered carbonyl iron sintered in H_2 for 18 hr. at 1500°C	12.7	13.6	14.6	16.7	16.8	16.3	16.1	16.5
B. Powdered carbonyl iron melted in H_2	12.7	13.8	14.6	16.6	16.8	15.8	15.2	14.9

pure iron. In all but three of the specimens the change in length in passing from face-centered to body-centered cubic lattice on cooling was greater than the reverse change on heating. The cause of this discrepancy is not certain and is being further investigated.

Ebert[3] has shown that below 0° the thermal expansion of iron can be computed with reasonable accuracy from heat capacity data by means of Grüneisen's equation:

$$\alpha_t=\frac{1}{l_0}\frac{\partial l}{\partial t}=\left(\frac{\partial E}{\partial T}\right)_P \Big/ 3Q_0\left[1-\frac{m+n+3}{6}\cdot\frac{E}{Q_0}\right]^2,$$

where

$$E=\int_0^T C_v dT, \quad Q_0=\left(\frac{C_p v}{(1/v)(dv/dT)}\right)_{T=0}$$

and m and n are exponents in the equation for the force between atoms. Taking $Q_0=170$ kcal. $(m+n+3)/6=3.8$ and deriving E and $\partial E/\partial T$ by assuming a characteristic frequency of 400, all of which numerical values were used by Ebert, we find that the calculated coefficients for high temperatures are in very poor agreement with those observed, a result which is not surprising since it is well known that the heat capacity of iron at high temperatures cannot be represented by a single Debye function. The equation predicts, however, that the ratio of α_t to C_p should be constant with temperature, a relation which is tested in Fig. 2 by using the expansion coefficients of sample *A* and the heat capacity data selected by Austin.[4] It is evident that proportionality continues with reasonable accuracy until the effects of the magnetic inversion begin to appear. Grüneisen's relation seems, therefore, not to be valid for ferromagnetics near the Curie point, at least insofar as macroscopic expansion is concerned. Whether true lattice expansion, determined precisely by refined x-ray methods, would give closer agreement remains to be seen.

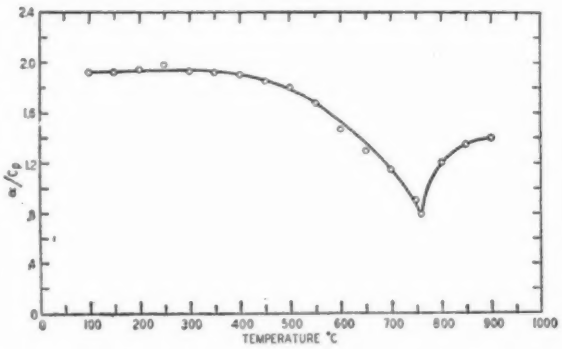

FIG. 2. Ratio of expansion coefficient to specific heat for iron plotted as a function of temperature.

The details of this investigation will appear in the *Transactions of the American Society for Steel Treating*.

[3] Ebert, Zeits. f. Physik **47**, 712 (1928).

[4] Austin, Ind. Eng. Chem. **24**, 1225 (1932).

An Inverse Boundary Value Problem in Electrodynamics

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From knowledge of the electromagnetic field at the surface of a half-space due to a prescribed oscillatory source, is determined the unknown variation with depth of the conductivity and the dielectric constant. Unique solutions exist for these quantities.

INTRODUCTION

IN THE inverse type of boundary value problem here considered, it is assumed that a given differential relationship is satisfied by a space field; that values of this field are prescribed over the boundary of a region; but that the differential relationships involve certain physical properties of material which are unknown functions of position. The problem is inverse in that one seeks to determine unknown physical properties of the region from a knowledge of the field on the boundary, rather than to obtain the field from a knowledge of physical properties. Such problems are fundamental in certain applications of physics, for example,[1] in the theory of geophysical prospecting, where it is desired to interpret the observed surface readings of a space field in terms of concealed geology. But, with a few exceptions, they are non-unique, and consequently the interpretation of the observational data is necessarily subject to basic uncertainties. However, unique solutions for two of the more simple problems of this character are available. Both, as might be expected, relate to a region in which the pertinent properties of the material are functions of one coordinate only, the depth. These two problems are (1) the interpretation, under the ray concept, of travel-time curves due to a seismic pulse;[2] and (2) the interpretation of a direct-current flow from a point electrode at the surface of a half-space of varying conductivity.[3] The present paper deals with the interpretation of the electromagnetic field produced by an oscillatory magnetic source situated at the surface of a plane earth whose conductivity and dielectric constant are unknown functions of depth.[4]

§1.0. FORMULATION OF THE PROBLEM

On the surface of a half-space whose unknown conductivity and dielectric constant vary only with depth, is located an electromagnetic source, consisting of concentric circular current sheets centering at the origin and varying in intensity with radial distance in a manner to be assigned. In time, the source currents vary harmonically with frequency $\omega/2\pi$. The direct problem for a dipolar source and a constant conductivity is customarily set up in terms of a wave equation and a Hertzian potential function. However, it seems more convenient for present purposes to treat the problem in terms of the field equations directly, and for the case of a more general type of source. Cylindrical coordinates ρ, ϕ, z will be used.

It is clear from symmetry that the component B_ϕ of the magnetic vector is everywhere zero. Similarly, the components E_ρ and E_z of the electric vector must vanish at all points. Since

[1] It appears possible that certain types of inverse boundary value problems will find application in the study of plasma.

[2] See G. Herglotz, Phys. Zeits. **8**, 145 (1907). Wiechert and Geiger, Phys. Zeits. **11**, 294 (1910). H. Witte, *Nachrichten der Gesellschaft der Wissenschaften zu Göttingen*, p. 199 (1932). L. B. Slichter, Physics **3**, 273 (1932).

[3] R. E. Langer, Bull. Am. Math. Soc. **39**, 184 (1933). L. B. Slichter, Physics **4**, 307 (1933).

[4] The corresponding direct problem for a dipolar source and an earth of constant conductivity has been treated by Sommerfeld and others. See A. Sommerfeld, Ann. d. Physik [4], **81**, 1135 (1926).

the dependence of the vectors E and B upon time is sinusoidal, we set, as usual,

$$E=R\{E_1 \exp j\omega t\}, \quad B=R\{B_1 \exp j\omega t\},$$

where E_1 and B_1 are now functions of position only. Then the two Maxwell circuital relations for the three nonvanishing components of the vectors E_1 and B_1 are the following,[5] where, for convenience, these last subscripts will henceforth be omitted:

$$\frac{\partial}{\partial z}\left(\frac{B}{\mu}\right)_\rho - \frac{\partial}{\partial \rho}\left(\frac{B}{\mu}\right)_z = \frac{4\pi}{c}\left(\sigma + j\frac{\epsilon\omega}{4\pi}\right)E_\phi \quad (1.1)$$

$$\partial E_\phi/\partial z = +j(\omega/c)B_\rho \quad (1.2)$$

$$\partial E_\phi/\partial \rho + E_\phi/\rho = -j(\omega/c)B_z. \quad (1.3)$$

In addition,

$$\text{div } B=0; \quad \text{div } \epsilon E=4\pi\rho. \quad (1.4)$$

But the latter equations, (1.4), are automatically satisfied under the symmetry postulated whenever the circuital relations are fulfilled. For simplicity, let it be assumed that $\mu=1$.

The boundary conditions to be associated with these equations are the following: At $z=0$, both E_ϕ and B_z are continuous; B_ρ however possesses a discontinuity at $z=0$ determined by the surface currents of the source in accordance with the equation,

$$(B_\rho)_{+z} - (B_\rho)_{-z} = (4\pi/c)l(\rho), \quad (1.5)$$

where $l(\rho)$ is the amplitude of the surface current. At infinity, the field vectors vanish at least as rapidly as in a spherically diverging electromagnetic wave; that is, as $1/r^2$.

§2.0. The Solution for E_ϕ

After introducing the notations:

$$s(z) \equiv (\sigma(z) + j\epsilon(z)\omega/4\pi)4\pi/c; \quad q \equiv j\omega/c \quad (2.1)$$

and substituting from Eqs. (1.2) and (1.3) into (1.1), we obtain

$$\frac{\partial^2 E}{\partial z^2} + \frac{\partial^2 E}{\partial \rho^2} + \frac{1}{\rho}\frac{\partial E}{\partial \rho} - \left(\frac{1}{\rho^2} + qs(z)\right)E = 0, \quad (2.2)$$

where E is now written for E_ϕ without confusion. The substitution $E=R(\rho)Z(z)$ separates the variables and yields the Bessel's equation,

$$\ddot{R}(\rho) + (1/\rho)\dot{R}(\rho) + (\lambda^2 - 1/\rho^2)R(\rho) = 0, \quad (2.3)$$

and the equation,

$$\ddot{Z} - (\lambda^2 - \epsilon\omega^2/c^2 + jb(z))Z = 0, \quad (2.4)$$

where

$$b(z) \equiv 4\pi\omega\sigma(z)/c^2.$$

Above the ground's surface, $z<0$, Eq. (2.4) takes the form.

$$\ddot{Z} - (\lambda^2 - \omega^2/c^2)Z = 0, \quad (2.5)$$

whence, if $k_0^2 \equiv \omega^2/c^2$,

$$Z = \exp\{\pm(\lambda^2 - k_0^2)^{\frac{1}{2}}z\}. \quad (2.6)$$

Since E and B remain finite at $\rho=0$, the appropriate solution of Eq. (2.3) is $R=J_1(\lambda\rho)$. Let a solution of (2.4) which vanishes at infinity be denoted by $Z_1(z, \lambda)$. Further characteristics of this solution will be developed presently. For positive values of z, the solution for E will be denoted by E_+, for negative z, by E_-. Let us seek solutions of type,

$$E_+ = \int_0^\infty J_1(\lambda\rho)F_1(\lambda)Z_1(z, \lambda)d\lambda \quad (2.7)$$

$$E_- = \int_0^\infty J_1(\lambda\rho)F_2(\lambda)\exp[+(\lambda^2 - k_0^2)^{\frac{1}{2}}z]d\lambda \quad (2.8)$$

where the functions $F_1(\lambda)$ and $F_2(\lambda)$ are such as to secure the satisfaction of the boundary conditions and the convergence of the integrals. The continuity of E at $z=0$, independently of ρ, implies that $F_2(\lambda) = F_1(\lambda)Z_1(0, \lambda)$, a relation which also assures the satisfaction of the continuity condition on B_z. The remaining condition at the surface, namely Eq. (1.5), may be written

$$(\partial E_+/\partial z)_{+0} - (\partial E_-/\partial z)_{-0} = j4\pi\omega l/c^2,$$

[5] The customary Gaussian system of units will here be used. The conductivity, σ and electric vector, E are in electrostatic units, the magnetic vector B in electromagnetic units.

that is,

$$\int_0^\infty J_1(\lambda\rho)F_1(\lambda)\{\dot{Z}_1(0,\lambda)-Z_1(0,\lambda)(\lambda^2-k_0^2)^{\frac{1}{2}}\}d\lambda=j\frac{4\pi\omega l(\rho)}{c^2}. \tag{2.9}$$

From this equation the required function $F_1(\lambda)$ may always be determined, when the source function $l(\rho)$ is given, by application of the Fourier-Bessel integral theorem. In the present case, we are particularly interested in a source which is of dipolar type at large distances. Within this limitation, then, we shall assign the function $l(\rho)$ in accordance with analytical convenience. A suitable choice is suggested by the discontinuous integral,[6]

$$\begin{aligned} a\int_0^\infty J_\nu(\lambda a)J_{\nu-1}(\lambda\rho)d\lambda &= (\rho/a)^{\nu-1};\quad 0<\rho/a<1\\ &=\tfrac{1}{2};\quad \rho/a=1\\ &=0;\quad \rho/a>1. \end{aligned}$$

Whence, if $\nu=2$, and if the source is such that

$$l=\rho/a,\ 0<\rho<a;\quad l=\tfrac{1}{2},\ \rho=a;\quad l=0,\ \rho>a;$$

then the boundary condition (2.9) will be satisfied provided $F_1(\lambda)$ is determined by the condition,

$$jJ_2(\lambda a)(4\pi\omega a/c^2)=F_1(\lambda)\{\dot{Z}_1(0,\lambda)-Z_1(0,\lambda)(\lambda^2-k_0^2)^{\frac{1}{2}}\}. \tag{2.10}$$

Thus, finally, the desired solution for E_+ is

$$E_+=j\frac{4\pi\omega a}{c^2}\int_0^\infty \frac{J_2(\lambda a)J_1(\lambda\rho)Z_1(z,\lambda)d\lambda}{\dot{Z}_1(0,\lambda)-(\lambda^2-k_0^2)^{\frac{1}{2}}Z_1(0,\lambda)}. \tag{2.11}$$

Assuming for the moment the uniform convergence of the integrals, the following expressions for B_z and B_ρ are derived from Eqs. (1.2) and (1.3):

$$B_\rho=\frac{4\pi a}{c}\int_0^\infty \frac{J_2(a\lambda)J_1(\rho\lambda)\dot{Z}_1(z,\lambda)d\lambda}{\dot{Z}_1(0,\lambda)-Z_1(0,\lambda)(\lambda^2-k_0^2)^{\frac{1}{2}}}, \tag{2.12}$$

$$B_z=-\frac{4\pi a}{c}\int_0^\infty \frac{J_2(a\lambda)J_0(\rho\lambda)Z_1(z,\lambda)\lambda d\lambda}{\dot{Z}_1(0,\lambda)-Z_1(0,\lambda)(\lambda^2-k_0^2)^{\frac{1}{2}}}. \tag{2.13}$$

As a check, this latter formula may be compared with Sommerfeld's[4] result for a vertical magnetic dipole above an earth of constant conductivity. If σ and ϵ are constant, and $k_1^2=\epsilon_1\omega^2/c^2-j4\pi\omega\sigma_1/c^2$, then

$$Z_1=\exp\{-(\lambda^2-k_1^2)^{\frac{1}{2}}z\}$$

and Eq. (2.13) becomes

$$B_z=\frac{4\pi a}{c}\int_0^\infty \frac{J_2(a\lambda)J_0(\rho\lambda)\exp[-(\lambda^2-k_1^2)^{\frac{1}{2}}z]\lambda d\lambda}{(\lambda^2-k_1^2)^{\frac{1}{2}}+(\lambda^2-k_0^2)^{\frac{1}{2}}}.$$

If Sommerfeld's expression for the Hertzian potential is formally differentiated under the integral sign, a factor λ^2 replaces the $J_2(a\lambda)$ above. Hence the integral diverges when $z=0$, and a check is clearly impossible. But for small values of λ and a, a formal resemblance between the formulae is apparent on account of the relation $J_2(a\lambda)\to a^2\lambda^2/8$.

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[6] N. Nielson, *Handbuch der Theorie der Cylinder Funktionen*, Teubner, 1904, p. 200.

§3.0 Validity of the Integrals for B_ρ and B_z

Granting, for the moment, the convergence of the formula (2.11) for E, it is desired to show that the integrals (2.12) and (2.13) do in fact represent the quantities B_ρ and B_z in accordance with their previous defining Eqs. (1.2) and (1.3); that is to say it is desired to establish the uniform convergence of the integrals (2.12) and (2.13).

Firstly it will be shown that the integrands in Eqs. (2.12) and (2.13) are bounded for all ρ and z, and for all real, finite, positive values of λ, i.e., that the quantities,

$$(A)\quad \frac{\lambda Z_1(z,\lambda)}{Z_1(0,\lambda)}\left\{\frac{1}{\dot{Z}_1(0,\lambda)/Z(0,\lambda)-(\lambda^2-k_0^2)^{\frac{1}{2}}}\right\},\qquad (B)\quad \frac{-\dot{Z}_1(z,\lambda)}{Z_1(0,\lambda)}\left\{\frac{1}{\dot{Z}_1(0,\lambda)/Z_1(0,\lambda)-(\lambda^2-k_0^2)^{\frac{1}{2}}}\right\},$$

are bounded.

To see this, set $Z=R\exp\left[i\int\beta(z,\lambda)dz\right]$ in Eq. (2.4), with R, β, real. Then

$$\ddot{R}-(\lambda^2-\epsilon\omega^2/c^2+\beta^2)R=0, \tag{3.1}$$

$$\dot{\beta}+2(\dot{R}/R)\beta-b(z)=0. \tag{3.2}$$

If, as it will be shown, the coefficient of R in Eq. (3.1) is always positive, then a positive monotonically decreasing solution of Eq. (3.1) is known to exist. The positive nature of this coefficient will first be postulated, and it will then be shown that a solution of Eq. (3.2) for β which insures the realization of this hypothesis can always be found. Then, since $R>0$, Eq. (3.2) has no singularities except at infinity, hence possesses the general integral,

$$\beta(z,\lambda)=\frac{1}{R^2(z,\lambda)}\left[f(\lambda)+\int_0^z b(\xi)R^2(\xi,\lambda)d\xi\right]. \tag{3.3}$$

Now suppose for large z, $\epsilon=\epsilon_2$, $\sigma=\sigma_2$ (constants). Then

$$Z_1=\exp\left[-z(\lambda^2-k_2^2)^{\frac{1}{2}}\right], \tag{3.4}$$

where

$$k_2^2\equiv\epsilon_2\omega^2/c^2-j4\pi\omega\sigma_2/c^2$$

or

$$Z_1=R_2\exp i\beta_2 z, \tag{3.5}$$

with

$$R_2=\exp\left[-\left\{(\lambda^2-\epsilon_2\omega^2/c^2)^2+(4\pi\,\omega\sigma_2/c^2)^2\right\}^{\frac{1}{4}}\cos(\psi/2)\right] \tag{3.6}$$

$$\beta_2=-\left\{(\lambda^2-\epsilon_2\,\omega^2/c^2)^2+(4\pi\,\omega\sigma_2/c^2)^2\right\}^{\frac{1}{4}}\sin(\psi/2). \tag{3.7}$$

Here

$$\tan\psi=4\pi\omega\sigma_2/(\lambda^2c^2-\epsilon_2\omega^2).$$

As λ ranges from zero to infinity ψ may be chosen to decrease from $\psi_0<\pi$ to zero. Thus $\sin(\psi/2)$ and $\cos(\psi/2)$ are always positive; β_2 is always negative, vanishes as $-1/\lambda$ for large λ, and is independent of z. Now the solution for $\beta(z,\lambda)$, as expressed by Eq. (3.3) must approach $\beta_2(\lambda)$ for large values of z. In the right member of Eq. (3.3), the numerator is an *increasing* function of z, since the integrand is positive. The denominator is a decreasing function, hence $\beta(z)$ steadily increased with z, and eventually approaches the negative constant (as to z), $\beta_2(\lambda)$. Hence $\beta(z,\lambda)$ is always negative, and $\beta^2(z,\lambda)\geqq\beta_2^2(\lambda)$. Hence in Eq. (3.1) the coefficient $\lambda^2-\epsilon\omega^2/c^2+\beta^2\geqq\lambda^2-\epsilon\omega^2/c^2+\beta_2^2$, where, from Eq. (3.7), the right member is a minimum for $\lambda=0$. It follows that the coefficient is assuredly positive when ϵ_2 and σ_2 are so assigned that

$$\epsilon(z)\{\epsilon(z)-\epsilon_2\}<4\pi^2\sigma_2^2/\omega^2$$

or, more simply, when $\epsilon<\epsilon_2$. Either condition may be considered to be satisfied at great depths without essential restriction on the physical problem. Thus both R and β decrease in absolute value as z increases; R remains positive, β negative, and $\beta\leqq\beta_2$.

Now in the quantity (B), the factor,

$$\dot{Z}_1(z)/Z_1(0) = \{\dot{R}(z)/R(0) + i\beta(z)R(z)/R(0)\} \exp\left(i\int_0^z \beta dz\right),$$

has an absolute value not greater than $((\dot{R}(0)/R(0))^2+\beta^2(0))^{\frac{1}{2}}$. Also, the absolute value of the denominator of the second factor,

$$|Z_1'(0)/Z_1(0) - (\lambda^2-k_0^2)^{\frac{1}{2}}| = |\dot{R}(0)/R(0) + i\beta(0) - (\lambda^2-k_0^2)^{\frac{1}{2}}|,$$

is at least as great as the absolute value of its imaginary component, $|\beta(0)| \geqq |\beta_2|$. A similar argument obviously applies to the function (A). Hence

$$\int_0^{\lambda_1} J_2(\lambda a) J_i(\lambda\rho) \begin{Bmatrix}(A)\\(B)\end{Bmatrix} d\lambda, \quad i=0, 1$$

are proper integrals.

When λ is sufficiently large (say $\lambda \geqq \lambda_1$) then from Eq. (2.4) $Z_1 \sim e^{-\lambda z}$ and the quantities (A) and (B) are asymptotically constants. Hence the integrals,

$$\int_{\lambda_1}^{\infty} J_2(\lambda a) J_i(\lambda\rho) \begin{Bmatrix}(A)\\(B)\end{Bmatrix} d\lambda,$$

are essentially

$$\int_{\lambda_1}^{\infty} J_2(a\lambda) J_i(\rho\lambda) e^{-\lambda z} d\lambda, \quad i=0, 1.$$

which converge uniformly for $z \geqq z_1 > 0$. Thus the integrals

$$\int_0^{\infty} J_2(a\lambda) J_i(\rho\lambda) \begin{Bmatrix}(A)\\(B)\end{Bmatrix} d\lambda$$

have been shown to converge uniformly when $z \geqq z_1 > 0$, and the formula (2.12) is valid when $z \geqq z_1 > 0$. Now

$$\int_0^{\lambda_1} J_2(a\lambda) J_i(\rho\lambda) \begin{Bmatrix}(A)\\(B)\end{Bmatrix} d\lambda$$

is continuous at $z=0$, and it is known[7] that the same is true of

$$\int_{\lambda_1}^{\infty} J_2(a\lambda) J_i(\rho\lambda) e^{-\lambda z} d\lambda; \quad \rho \neq a.$$

Thus the right members of Eqs. (2.12) and (2.13) are continuous at $z=0+$. Since the left members are also continuous at $0+$, the equalities (2.12) and (2.13) have been established for $z \geqq 0$.

The similar integral (2.11) for E can be shown to converge by the same argument, so that the assumption introduced at the beginning of §3.0 is justified.[8]

§4.0. Inversion of the Formulae for B_ρ and B_z

From Eqs. (2.12) and (2.13), the expressions for B_ρ and B_z at the ground's surface are

$$B_\rho(\rho, 0) = \int_0^{\infty} J_1(\lambda\rho) k_\rho(\lambda) d\lambda \tag{4.1}$$

[7] G. N. Watson, *Theory of Bessel Functions*, Cambridge University Press, 1922, p. 399.

[8] The writer is indebted to Professor R. E. Langer for his helpful criticism of §3.0 in manuscript.

$$B_z(\rho, 0) = \int_0^\infty J_0(\lambda\rho) k_z(\lambda) d\lambda, \tag{4.2}$$

where

$$k_\rho(\lambda) \equiv (4\pi a/c) J_2(\lambda a) \dot{Z}_1(0, \lambda) / [\dot{Z}_1(0, \lambda) - Z_1(0, \lambda)(\lambda^2 - k_0^2)^{\frac{1}{2}}] \tag{4.3}$$

$$k_z(\lambda) \equiv (-4\pi a/c) J_2(\lambda a) \lambda Z_1(0, \lambda) / [\dot{Z}_1(0, \lambda) - Z_1(0, \lambda)(\lambda^2 - k_0^2)^{\frac{1}{2}}] \tag{4.4}$$

are in general complex numbers which approach a real limit (see §3.0) as λ becomes large. Let the real and imaginary parts of the four quantities above be designated by notations of the type,

$$k_\rho(\lambda) \equiv k_\rho'(\lambda) + jk_\rho''(\lambda), \quad \text{etc.}$$

If it be assumed that the quantities B_ρ', B_ρ'', B_z' and B_z'' at the surface are known by observation at all distances from the source, then the four functions $k_\rho'(\lambda), \cdots, k_z''(\lambda)$, may each be determined by inverting Eqs. (4.1) and (4.2) in accordance with the Fourier-Bessel integral theorem.[9] This theorem states in effect that

$$F(r) = \int_0^\infty J_\nu(\mu r) \mu d\mu \int_0^\infty F(R) J_\nu(\mu R) R dR,$$

provided

$$\int_0^\infty F(R) R^{\frac{1}{2}} dR$$

is absolutely convergent.

Hence $B_\rho', \cdots, B_z''$ satisfy formulae of the type,

$$B_\rho'(0, \rho) = \int_0^\infty J_1(\lambda\rho) \lambda d\lambda \int_0^\infty B_\rho'(0, \xi) J_1(\lambda\xi) \xi d\xi, \tag{4.5}$$

provided the functions $k_\rho', \cdots, k_z''$ are expressed by the equations:

$$k_\rho'(\lambda) = \lambda \int_0^\infty B_\rho'(0, \rho) J_1(\lambda\rho) \rho d\rho \tag{4.6a}$$

$$k_\rho''(\lambda) = \lambda \int_0^\infty B_\rho''(0, \rho) J_1(\lambda\rho) \rho d\rho \tag{4.6b}$$

$$k_z'(\lambda) = \lambda \int_0^\infty B_z'(0, \rho) J_0(\lambda\rho) \rho d\rho \tag{4.6c}$$

$$k_z''(\lambda) = \lambda \int_0^\infty B_z''(0, \rho) J_0(\lambda\rho) \rho d\rho \tag{4.6d}$$

and provided that the integrals of type,

$$\int_0^\infty B_\rho'(0, \rho) \rho^{\frac{1}{2}} d\rho,$$

are absolutely convergent. Since B is everywhere finite and vanishes at infinity as $1/\rho^2$, this latter condition is always satisfied. Thus it follows from Eqs. (4.3) and (4.4) that

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[9] G. N. Watson, *Theory of Bessel Functions*, §14.4, Cambridge University Press, 1922.

$$\frac{k_\rho(\lambda)}{k_z(\lambda)}=-\frac{\dot{Z}(0,\lambda)}{\lambda Z(0,\lambda)}=\frac{\int_0^\infty B_\rho'(0,\rho)J_1(\lambda\rho)\rho d\rho+j\int_0^\infty B_\rho''(0,\rho)J_1(\lambda\rho)\rho d\rho}{\int_0^\infty B_z'(0,\rho)J_0(\lambda\rho)\rho d\rho+j\int_0^\infty B_z''(0,\rho)J_0(\lambda\rho)\rho d\rho}, \tag{4.7}$$

where the quantities occurring in the integrands may all be considered known. Yet it should be noted that the experimental observation of the real and imaginary parts of the B vector involves the difficult measurement of the phase of the vector with respect to the source current.[10] However, it seems desirable to suppress questions of observational technique at present, since our primary object is the examination of the theoretical nature of the interpretation problem. We assume, then, that the function $-\dot{Z}_1(0,\lambda)/\lambda Z(0,\lambda)$ which we shall denote by $K(\lambda)$ and refer to as the "kernel," is *known*.[11] It is clear that this function embodies, and is precisely equivalent to, the totality of observational data at the boundary $z=0$. For, on the one hand, knowledge of $B_\rho(0,\rho)$ and $B_z(0,\rho)$ suffices to define $K(\lambda)$. Conversely, knowledge of $K(\lambda)$ determines both $B_\rho(0,\rho)$ and $B_z(0,\rho)$ through Eqs. (4.1) to (4.4) inclusive. A convenient method due to Langer[3] may now be applied for determining the unknown conductivity function from knowledge of the kernel and the form of the differential Eq. (2.4).

§5.0. Determination of the Conductivity and Dielectric Constant from the Kernel

It is evident that the solution, $Z_1(z,\lambda)$, of Eq. (2.4), is of the form,

$$Z_1(z,\lambda)\sim e^{-\lambda z}, \tag{5.1}$$

for large values of λ. Consequently the kernel,

$$K(\lambda)\equiv-\dot{Z}_1(0,\lambda)/\lambda Z_1(0,\lambda), \tag{5.2}$$

approaches unity at infinity. Therefore for large λ this function admits of the expansion,

$$K(\lambda)\sim\sum_{n=0}^{\infty}a_n\lambda^{-n}, \tag{5.3}$$

where $a_0=1$, and the other constants are to be considered known, since $K(\lambda)$ is known. They are in general complex.

If the substitution $v(z,\lambda)\equiv-\dot{Z}_1(z,\lambda)/Z_1(z,\lambda)$ be introduced into the differential Eq. (2.4), $v(z,\lambda)$ is seen to satisfy the Riccati equation,

$$\dot{v}-v^2+\{\lambda^2-k_1^2+jb(z)\}=0, \tag{5.4}$$

where

$$k_1^2\equiv\epsilon(z)\omega^2c^2.$$

Also, in view of (5.1), (5.2) and (5.3), $v(z,\lambda)$ possesses an asymptotic expansion of the form,

$$v(z,\lambda)\sim\lambda\sum_{n=0}^{\infty}\alpha_n(z)\lambda^{-n}, \tag{5.5}$$

where

$$\alpha_0=1, \tag{5.6}$$

and each coefficient satisfies the boundary condition,

$$\alpha_i(z)\to a_i \quad \text{as} \quad z\to 0, \tag{5.7}$$

and is analytic in the interval $(0,\infty)$. Substitution of the expression (5.5) for $v(z,\lambda)$ into Eq. (5.4) leads to the relation,

$$\sum_{n=-1}^{\infty}\beta_n\lambda^{-n}=jb(z)-k_1^2(z), \tag{5.8}$$

where the coefficients β_n are given by the formula,

$$\beta_n=-\dot{\alpha}_{n+1}+\sum_{r=0}^{n+2}\alpha_{n+2-r}\alpha_r. \tag{5.9}$$

But the right member of Eq. (5.8) is independent of λ. Hence each β_n except β_0 must vanish. Thus

$$\dot{\alpha}_{n+1}=\sum_{r=0}^{n+2}\alpha_{n+2-r}\alpha_r; \quad n\neq 0. \tag{5.10}$$

For $n=-1$, this yields

$$\dot{\alpha}_0=2\alpha_1=0$$

by Eq. (5.6), and consequently, for $n=0$, we have

$$jb(z)-k_1^2(z)=2\alpha_2(z). \tag{5.11}$$

[10] Apparently the experimental determination of phase is most readily accomplished by transmitting the time signals by an auxiliary high frequency wave. When the frequency term is high relative to the conductivity term (see Eq. 2.4) the velocity of propagation is practically independent of the subsoil.

[11] The integrals occurring in Eq. (4.7) are of a type readily evaluated by the Bush Mechanical Integraph; V. Bush, J. Frank. Inst. **212**, 447 (1931).

Eq. (5.10) expresses the derivatives $\alpha_i'(z)$ in terms of the functions $\alpha_i(z)$ themselves. Indirectly it yields corresponding expressions for the higher derivatives, $\alpha_i^{(n)}(z)$ as well. Now the functions $\alpha_i(z)$ are all known at $z=0$, through the relations (5.7); hence the MacLaurin series expansion of each of the functions α_i is computable. In particular, the first several coefficients in the expansion for $\alpha_2(z)$ are the following:

$$\alpha_2(0)=a_2,$$

$$\dot{\alpha}_2(0)=2a_3,$$

$$\ddot{\alpha}_2(0)/2!=2a_4+a_2^2,$$

$$\dddot{\alpha}_2(0)/3!=4a_5/3+8a_3a_2/3,$$

$$\alpha_2^{(4)}(0)/4!=2a_6/3+2a_2a_4+5a_3^2/3+2a_2^3/3,$$

. . . . . .

The function $\alpha_2(z)$ may thus be computed. By equating real and imaginary parts in Eq. (5.11) both the quantities $b(z)$ and $k_1(z)$ are obtained; that is, the desired computation of the conductivity function as well as the dielectric constant has been effected. It is to be noted that the calculation of the conductivity function, $b(z)$, from $\alpha_2(z)$ necessitates definite knowledge of the *imaginary* part of $\alpha_2(z)$, and consequently of the real and imaginary parts, B' and B'', in Eq. (4.7). In other words, if the observational data are restricted to points so near the source that the phase change is inappreciable, then, *ipso facto*, the computation of the variation of conductivity with depth is impossible.

In the case of a symmetrically anisotropic medium, whose conductivity components σ_ρ and σ_z vary only with z, it is clear that only the horizontal component σ_ρ is effective in the present problem, since the secondary currents are confined to horizontal planes.

It will be noticed that the interpretation problem has been solved without explicit utilization of the frequency; however knowledge of *both* B_z and B_ρ has been presumed. If, as is usual, the frequency $\omega/2\pi$ is known, then either Eq. (4.3) or (4.4) suffices to define the kernel,

$$-\dot{Z}_1(0,\ \lambda)/\lambda Z_1(0,\ \lambda).$$

It follows that $B_\rho(0)$ and $B_z(0)$ are mutually dependent, and that knowledge of either alone serves to define the other and to furnish unique solutions for the variation of the conductivity and of the dielectric constant with depth.

A Study of the Evaporation of Small Water Drops

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A theoretical expression for the evaporation of small spherical water drops in still air is developed from the general evaporation equation of Jeffreys. Experimental data for the evaporation of drops ranging from 25 to 2600 microns in diameter are obtained at several temperatures and relative humidities. After making approximate corrections for the cooling of the drops it is found that the results are in general agreement with the theoretical evaporation equation. Residual variations which are functions of the drop size and the difference between the water vapor density at the surface of the drop and at a distance from the drop are probably due to inaccuracies in the method used for computing the drop temperatures. The results of the paper furnish a means for computing the total time required for the complete evaporation of a drop of liquid water into a still atmosphere at any given temperature and relative humidity.

IN connection with the development of apparatus for the measurement of the liquid water content of a foggy atmosphere it was necessary to determine the time required for the evaporation of small water drops as a function of the drop size, the ambient temperature and the relative humidity. In view of the importance of this subject in other meteorological problems as well as in connection with air-conditioning and various industrial applications the results of this investigation are presented separately.

This study was undertaken primarily for application to the evaporation of fog drops and since their velocity with respect to the air is small (0.1 to 2.0 cm/sec.) the problem may be considered as essentially equivalent to the evaporation of a stationary drop into a still atmosphere. The case of larger drops falling freely in the air at a considerable velocity is more complex and is not considered in this paper.

One of the first theoretical attacks on the general problem of evaporation was made by Stefan[1] who obtained analytical expressions for two special cases. One was for the evaporation from a tube of fixed length and constant cross section and the other was for the evaporation from a flush circular area, both into a still atmosphere. Much more recently Jeffreys[2] has developed a more general solution which agrees essentially with Stefan's results. A search of the literature has failed to discover either a theoretical or experimental consideration of the evaporation of spherical drops but Jeffreys' solution may be readily applied to this case. Jeffreys considers the evaporation problem as essentially one of gaseous diffusion. The general diffusion equation is

$$\frac{dV}{dt}=\frac{\partial}{\partial x}\left(k\frac{\partial V}{\partial x}\right)+\frac{\partial}{\partial y}\left(k\frac{\partial V}{\partial y}\right)+\frac{\partial}{\partial z}\left(k\frac{\partial V}{\partial z}\right), \quad (1)$$

where V is the fraction of the air density at any point due to the water vapor (it is also called the concentration); t is the time; d/dt is the total differential following a particle of the fluid; and k is the coefficient of diffusion. For the special case of evaporation into still air from a small surface it is shown that the diffusion equation for a steady state is given by

$$\nabla^2 V=0, \quad (2)$$

where $\nabla^2=$ the Laplacian operator. Jeffreys now observes that this equation is also satisfied by the potential in electrostatic problems and he proceeds to solve it by analogy to the electrostatic case. The solution for the total diffusion outward from the surface is found to be

$$4\pi kC\rho(V_0-V) \text{ g/sec.}, \quad (3)$$

where C is the electrostatic capacity of the

[1] Stefan, Sitzb. Akad. Wiss. Wien. **66**, 385 (1873); **73**, 943 (1881).

[2] H. Jeffreys, Phil. Mag. **35**, 270 (1918).

evaporating surface; ρ the density of the air; and V_0 and V the water vapor concentrations at the surface and at a considerable distance from the surface respectively.

For the case of a sphere of diameter a the electrostatic capacity is $a/2$. If Vol is the volume of the sphere and δ is the density of the water the evaporation equation becomes

$$\delta \cdot [d(Vol)/dt] = -2\pi ka\rho(V_0 - V) \text{ g/sec.} \quad (4)$$

The rate of evaporation is thus proportional to the diameter of the sphere rather than to the surface. To facilitate computations it should be noted that the product of the concentration and the air density is the density of the water vapor and the above equation may be written

$$\delta \cdot [d(Vol)/dt] = -2\pi ka(D_0 - D) \text{ g/sec.,} \quad (5)$$

where D_0 is the water vapor density at the surface of the sphere; D the water vapor density at a considerable distance from the sphere.

It was the purpose of the experimental work described below to verify this theoretical expression and to indicate such modifications as are necessary. The drops were observed at rest suspended from fine wires or glass filaments within a small chamber in which the relative humidity could be maintained constant at any desired value. The entire apparatus was located in a temperature controlled room and the temperature changes were effected by varying the room temperature. The wires and glass filaments were made as small as possible in order to make their effect negligible. Since there is a definite lower limit to the size of drop which can be suspended from a support of a given diameter it was necessary to use supports of various sizes to cover the desired range of drop sizes. The diameter and material of the various supports and the range of drop diameters with which they were used are summarized in Table I. Overlapping evaporation readings were obtained with various supports and it was found that the effect of the size of the support was inappreciable within the limits given in the above table. Drops much larger than 2000 microns were found to deviate from a spherical form and drops smaller than 25 microns could not be accurately observed because of the limitation imposed by the size of the smallest available support. Care was taken in all cases to insulate the supporting wires from the metal portions of the evaporation chamber so that the drops would be free to assume a temperature different from the ambient temperature. To reduce the area of contact between the drop and the support as much as possible the supports were given a very thin coating of paraffin. The drops were formed from distilled water by special pipettes with very fine outlets and were then transferred to the support. The smallest drops which could be handled satisfactorily were about 300 microns in diameter.

TABLE I.

Material of support and diam. (microns)		Range of drop diam. (microns)
Glass	250	over 2000
Glass	85	2000 to 1000
Glass	25	1200 to 300
Platinum Wollaston Wire	2.5	500 to 25

The humidity within the chamber was maintained constant by means of solutions of various inorganic salts which were contained in the bottom. In this way relative humidities of 0, 42, 54, 66, 86.5, and 88.6 percent were obtained. A hair hygrometer was incorporated in the evaporation chamber to indicate when the humidity had reached a constant value and to detect small changes in relative humidity during a series of observations. The absolute values of the relative humidity maintained above the various solutions were determined in a separate chamber by means of an Assman psychrometer and a dew-point apparatus. A range of temperatures from 3° to 32°C was used.

The diameter of the drop under observation was measured by means of an ocular micrometer in a low power microscope. The drop was lighted from the side by a simple illuminator consisting of a 50 watt concentrated filament lamp, a single lens and a cell containing a ten percent solution of copper sulphate to remove the heat. The effectiveness of this cell was tested by placing a thermometer with a blackened bulb in the beam and over a period of one-half an hour the temperature rise did not exceed 0.1°C above the ambient temperature. As a further check on this important point two drops of equal size were allowed to evaporate for a given time, one with

the light on continuously and the other with the light off. The two drops were found to evaporate at the same rate within the limits of accuracy of the measurements.

For a given temperature and relative humidity overlapping and duplicate data were obtained over a range of drop diameters from about 50 to 2000 microns and in some cases the measurements were extended to include drops as small as 25 and as large as 2600 microns. In general the procedure was to place as large a drop as possible on a given support and allow it to evaporate until it became so small that the support had an appreciable effect. Readings of the drop diameter were taken at intervals varying from one-half to ten minutes depending upon the rate of evaporation.

A group of typical drop evaporation curves is given in Fig. 1. It will be observed that all of the curves are apparently parabolic. We may readily develop the theoretical equation of these curves. Since

$$da/dt = (2/\pi a^2)d(Vol)/dt,$$

from Eq. (5):

$$\delta(da/dt) = -(4k/a)(D_0 - D). \qquad (6)$$

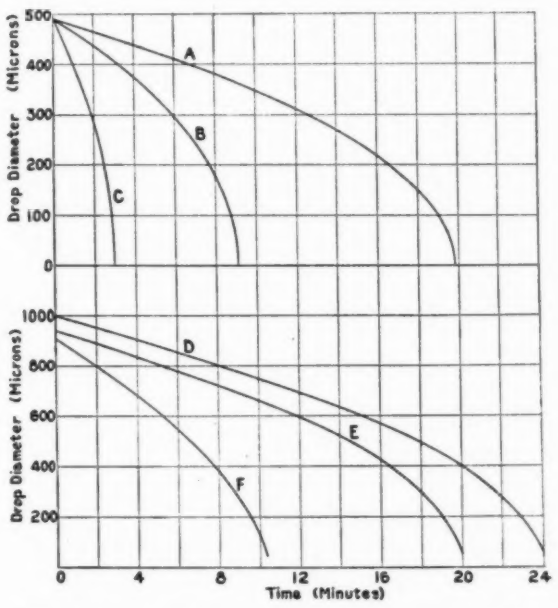

FIG. 1. Experimental curves for the evaporation of small water drops into a still atmosphere. *A*, 20.8°C, 88.6 percent relative humidity; *B*, 19.6°C, 53 percent relative humidity; *C*, 21.7°C, 0 percent relative humidity; *D*, 4.8°C, 0 percent relative humidity; *E*, 20.3°C, 42 percent relative humidity; *F*, 22.0°C, 0 percent relative humidity.

Integrating and letting A be the initial drop diameter and putting $\delta = 1$ for water,

$$a^2 = A^2 - 8k(D_0 - D)t, \qquad (7)$$

which is the equation of a parabola. If T is the intercept on the time axis or, in other words, the time required for the complete evaporation of the drop, Eq. (7) may be written as

$$a^2 = 8k(D_0 - D)(T - t). \qquad (8)$$

In Fig. 2 some of the data of Fig. 1 have been replotted on logarithmic paper with $(T-t)$ as abscissas. The dashed line has a slope of exactly two and the experimental curves have very nearly the same slope indicating that they deviate only slightly from true parabolas in accordance with Eq. (8). This, in turn, shows that the drop evaporation is proportional to the diameter.

It now remains to show that the evaporation is also proportional to $(D_0 - D)$. This is most readily done with the aid of Eq. (6) by plotting $a \cdot (da/dt)$ against $(D_0 - D)$. The values of da/dt were obtained directly from the experimental curves while D_0 and D are respectively the water vapor densities corresponding to saturation at the ambient temperature and to the particular relative humidity and temperature of the evaporation chamber. These data are plotted in Fig. 3. The dots represent points obtained at a constant relative humidity (0 percent) and variable temperature and the circles are from the data taken at constant temperature (20°C) and variable relative humidity. The two sets of data do not lie on the same curve and do not lie on a straight line as would be indicated by Eq. (5). Furthermore, the slope is considerably less than $4k$ if k is given its usual value of about 0.25 cm²/sec. The explanation of these discrepancies seems to lie in the fact that the drop cools to a temperature considerably lower than the ambient temperature due to the evaporation. The equilibrium temperature of the drop is evidently determined by a balance between the heat loss due to evaporation and the heat gained by radiation, conduction and convection. The exact analytic solution of this problem is, however, practically impossible because of the multiplicity of factors which are involved. The actual measurement of the temperature of drops as small as were used in this investigation is also difficult and was not at-

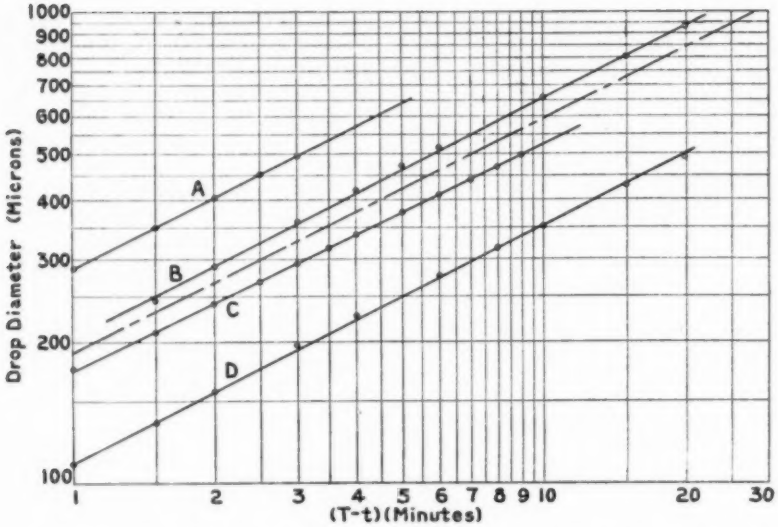

FIG. 2. Some of the data of Fig. 1 replotted on logarithmic paper with $(T-t)$ as abscissas. *A*, 21.7°C, 0 percent relative humidity; *B*, 20.3°C, 42 percent relative humidity; *C*, 19.6°C, 53 percent relative humidity; *D*, 20.8°C, 88.6 percent relative humidity.

tempted. A very similar problem which has received considerable attention is the measurement of the relative humidity by means of the temperature depression of a wet bulb thermometer. The so-called psychrometric formula has been developed for this case on the basis of certain theoretical considerations but it contains so many approximations and experimentally determined constants that it is little better than an empirical expression. However, considerable experimental work has been done on this subject and the results for ventilated wet bulb thermometers are probably quite accurate. Data for unventilated wet bulb thermometers are not in good agreement possibly because of differences in the experimental conditions since the thermometer would seldom be entirely unventilated unless enclosed in a chamber. In view of these variations, a wet bulb thermometer was prepared and inserted in the evaporation chamber in the position normally occupied by the drop. The temperature and relative humidity were then varied and the depression of the wet bulb thermometer noted. From these data the constant in the psychrometric equation was determined. For all values of relative humidity and ambient temperatures from 5° to 25°C the following equation holds quite well as long as the temperature of the wet bulb does not drop below 0°C:

$$e-e'=12.3\times10^{-4}B(\tau-\tau'), \qquad (9)$$

where τ is the ambient temperature in °C; τ', the temperature of the wet bulb thermometer

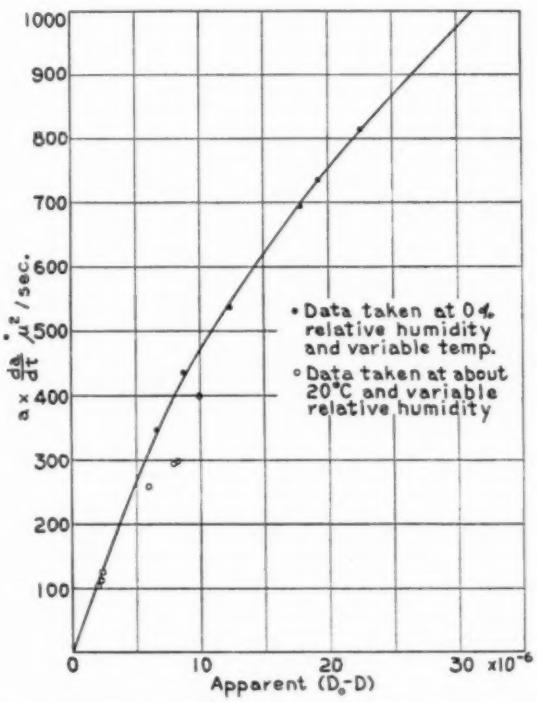

Fig. 3. The relation between the apparent density difference and the product of drop diameter and rate of change of drop diameter.

in °C; e, the vapor pressure in the chamber; e', the saturation vapor pressure corresponding to τ'; and B, the barometric pressure measured in same units as e and e'. For temperatures higher than 25°C the actual depression of the wet bulb thermometer was found to be somewhat greater than that given by the above expression. Although it is evident that these results cannot be expected to apply strictly to the water drops which are much smaller and of a different shape than the thermometer bulb and which are suspended in a different manner they will at least permit approximate drop temperatures to be computed.

Corrected drop temperatures were computed for all of the drop evaporation data on the basis of this psychrometric equation. D_0 then becomes the density corresponding to saturation at the corrected drop temperature. The data of Fig. 3 have been corrected in this manner and replotted in Fig. 4. It will be observed that all of the points lie very nearly on a straight line. The slope of this line is $0.72\times10^8\mu^2$/sec. giving a value of $k=0.18$ cm²/sec. This is somewhat lower than the accepted value of the diffusion coefficient. As given in the *International Critical Tables*, k is about 0.22 cm²/sec. at 0°C and 0.25 cm²/sec. at 20°C. Possible causes of this deviation are considered below.

Residual variations with a definite trend still remain after the correction for drop temperature has been made. Values of k have been computed from the data and plotted against drop diameter for various values of (D_0-D) in Fig. 5. It will be observed that the apparent value of k decreases for small drop diameters and for large values of (D_0-D) and that the maximum value corresponds very closely to the value of the diffusion coefficient at 20°C. This would seem to indicate that the actual drop temperatures were lower for small drops and large density differences than the temperature of the wet bulb thermometer. In view of the obvious differences in the two cases this discrepancy is not surprising. It might be possible to obtain a more satisfactory empirical expression for the drop temperature from the data of Fig. 5 by assuming a fixed value of k but this has not been done because it is not certain that the observed variations are entirely due to inaccuracies in computing the drop temperature.

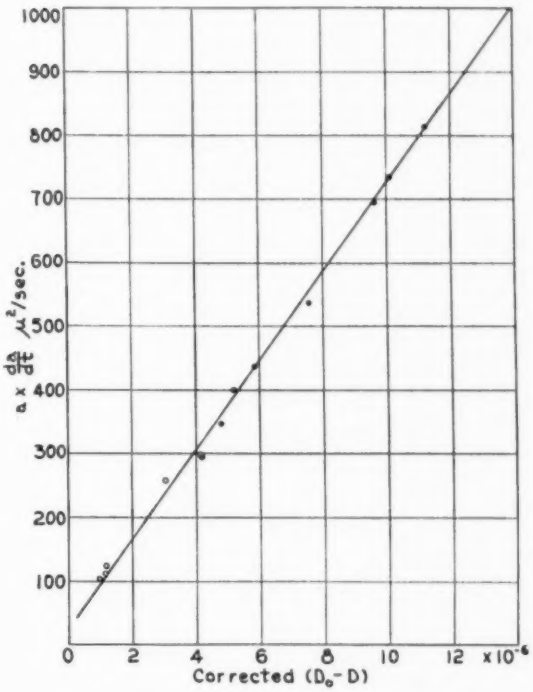

FIG. 4. The data of Fig. 3 replotted against a density difference obtained from the corrected drop temperatures.

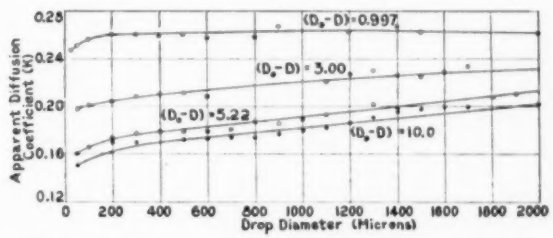

FIG. 5. The apparent diffusion coefficient as a function of drop size and density difference. ((D_0-D) values are $\times10^{-6}$.)

If T is the total time in seconds which is required for the complete evaporation of a drop of initial diameter A it follows from Eq. (7) that

$$T=A^2/8k(D_0-D). \qquad (10)$$

To compute from this expression it is first necessary to determine the corrected drop temperature from Eq. (8). D_0 and D may then be obtained from tables (density compared to water). An average value of k is then obtained from Fig. 5 and if A is expressed in centimeters Eq. (9) will give the total time in seconds required for the complete evaporation of the drop.

It has been noted earlier in this paper that this work was undertaken primarily for application to the problem of the evaporation of fog drops. The smallest drops which have been studied were about 25 microns in diameter and many fog drops are smaller than this.[3] It does not seem practicable to extend drop evaporation measurements to smaller drops by the methods of this paper but it is hoped that confirmatory data for small drops can be obtained in the near future by another method. In the meantime it is not thought that serious errors will be introduced if the curves of Fig. 5 are extended to include drops having a diameter as small as 5 or 10 microns. It is probable that the larger fog drops (20 to 40 microns) will evaporate somewhat more rapidly than the results of this paper would indicate because of their velocity with respect to the air. In connection with the application of the results of this paper to the evaporation of fog drops it is also important to remember that these measurements have been made on drops composed of distilled water whereas fog drops are usually composed of dilute salt solutions. For the fogs which are encountered along the southern coast of New England this salt content varies from 20 to 400 parts per million by weight. This salt content will have little effect at first but as the drop continues to evaporate the concentration of the salt will increase and will reduce the saturation vapor pressure and so retard the evaporation. If the relative humidity is sufficiently high a point will finally be reached where the vapor pressure at the surface of the drop will equal the vapor pressure in the air and evaporation will cease. In most cases this effect will probably be of little importance since the size of the drop when equilibrium is reached will usually be not much greater than the irreducible minimum size represented by the solid salt and dust which remain after complete evaporation. An effect which is very similar to the above will occur with very small drops of even pure water. This is due to the lowering of the saturation vapor pressure as the radius of curvature becomes very small. This effect is entirely inappreciable for drops greater than one micron in diameter and does not become of real importance until the drop is about one-tenth of a micron in diameter.

[3] H. G. Houghton, Physics **2**, 467 (1932).

The Final Distribution of Retained Liquid in an Ideal Uniform Soil

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If liquid, initially saturating the pores of a soil, is allowed to drain from that soil, no such complete drainage as occurs in a simple capillary tube is observed; large quantities of liquid are retained. The quantity of liquid held by the soil immediately after drainage gradually alters; it decreases to a stationary value and the liquid so held finally arranges itself in a stable distribution. Whatever be the distribution, the bounding liquid surfaces are capillary ones and subject to the laws of thermodynamics and capillarity; the Kelvin relation, in general determines the curvatures. The problem is considered for an ideal soil, that is an assemblage of spheres, of a single size, packed at random. There are in the ideal soil three types of distribution. First, there is a pendular region where the liquid is retained in the form of single rings of liquid wrapped around the axis of each pair of adjacent grains in contact. Second, there is a funicular region, which may be considered to arise by coalescence of the rings; we have two or more grain contacts imbedded in a single liquid mass, that is, webs of liquid enmeshing two or more grain contacts and which may involve many grains of the packing. There is, finally, a saturation region in which all pores are completely filled. The limits of each of these zones are determined. The funicular zone is a zone of hysteresis and all values between a normal minimum and complete saturation are usually possible. To calculate the normal minimum distribution the actual packing is replaced by an average packing of grains in hexagonal array and equally spaced to give the required porosity. The funicular distribution is now in the form of single rings wrapped around the axis of each pair of grains of the packing. The volume of each type of ring is determined in terms of $(\sigma/\rho ghr)$, where σ is the surface tension of the liquid and ρ its density, r the grain radius, and h the height of the ring above a free liquid reference plane. The average volume of each type of ring is obtained for all rings confined between two given planes. From the average ring volume and the number of such in each cc of packed space, the total retention in each zone above saturation is found. The distribution, that is, the liquid retained in any lamina at a height h above the free liquid, is also given. The results are compared with the data of King.

IT IS well known that a long column of soil, if its pores have been initially filled with liquid and then allowed to drain, retains considerable quantities of liquid; and no such complete drainage as occurs in a simple capillary tube, subjected to a similar process, takes place. If the soil column has been rapidly drained, large quantities of liquid, distributed throughout its entire length, will be found. If, now, the rapidly drained column is allowed to stand for several months, and then examined, the distribution of liquid will be observed to have undergone a great change; the upper parts of the column will be found to contain but the slightest traces of moisture, while the lower parts still retain considerable amounts. If the column is allowed to stand further, and examined at intervals, the distribution will be observed to become finally stationary. We may, on the other hand, suppose the drainage to have occurred very slowly and to have occupied a time equal to that covered by the whole of the experiment just described; the distribution will again become stationary, but the total retention may be less than that for rapid drainage. In either case, the distribution finally prevailing depends solely on the vapor pressures of the liquid, existing in the pore space during the final stages of the process; it is permanent and thermodynamically stable. We shall consider the final distribution for an assemblage of spheres of a single size, packed at random, that is, an ideal soil.

We shall, in order better to understand the nature of the final distribution, consider that the drainage of the ideal soil is performed under definitely controlled conditions. We suppose the soil to be packed in the column shown in Fig. 1a, in which it is supported by the gauze c. The system is kept at constant temperature and contains, besides the soil, only the liquid and its vapor. We suppose, finally, that all pores have been filled and drained, and that the system,

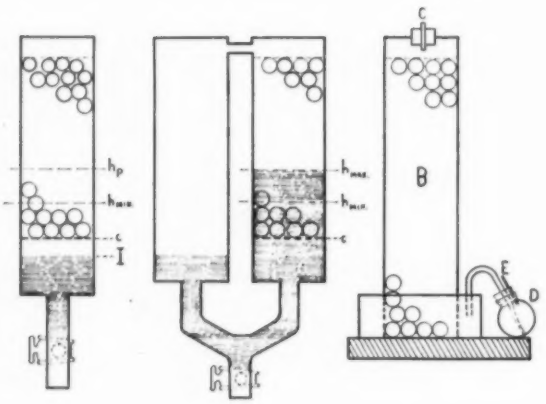

FIG. 1a. Single drainage column: I marks the free liquid surface; c is gauze supporting the soil; $h_{min.}$ marks the minimum height of rise and lower limit of saturation; h_P denotes the lower limit of the pendular zone.

FIG. 1b. Double column to show saturation hysteresis: $h_{min.}$ marks the minimum height of rise and $h_{max.}$ the maximum rise; the intervening interval is the region in which saturation hysteresis occurs.

FIG. 1c. Drainage column of King: B is the soil; D the collecting bottle; C and E are small capillaries.

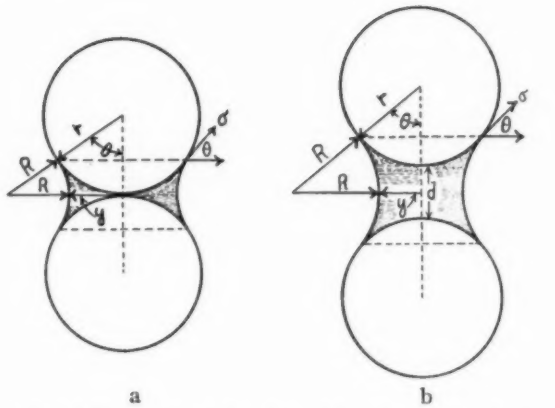

FIG. 2. (a) Simple pendular ring of liquid. (b) Simple ring of liquid in spaced hexagonal packing.

with the free surface of the liquid in a position just below the soil—marked I in the figure—has been allowed to come to equilibrium. It is convenient, now, to explore the drained column, throughout its length, and ascertain just how the liquid is distributed; whether in discrete masses, a continuous body or perhaps both. We shall consider this question in terms of the governing physics; the conclusions reached are easily confirmed by experiment.

If we examine the liquid retained in the upper parts of the soil column, we find it is in discrete masses and each mass is a ring of liquid wrapped around the contact point of a pair of adjacent grains as in Fig. 2a. Liquid must accumulate in these positions rather than in a uniform layer over the grain surfaces, otherwise the energy of the retained-liquid system would not be a minimum; the wetting layer, one molecule or so thick, is, of course, supposed to exist. As we proceed downward the rings increase in size until, finally, they begin to coalesce and merge into more complicated masses; we have, then, two or more contact points imbedded in a common liquid mass.

The single rings do not merge at a definite level of the column, but do so progressively as we descend further down. That this is so may be seen from the fact that the larger the angle between the axes of two adjacent pairs of grains, the larger the rings that can be supported; the axis of a pair of grains is defined as their line of centers, and is coincident with the axis of the ring. Now the angle between the axes of two adjacent grain pairs varies within definite limits because of the random nature of the packing; thus coalescence of rings begins first with those grain pairs whose axes are closest, and occurs lower in the column with rings whose axes make the larger angles. The more complicated masses grow as we descend until finally a stage is reached where they merge and form a capillary surface extending completely across the soil body; the pores below this surface are completely saturated.

We thus observe, as we descend the soil column, three types of liquid distribution. First, there is a stage with single liquid rings wrapped around grain pairs, with one contact point to a single mass—called by Versluys[1] the pendular stage. Second, there is a stage where the single rings are combined, in general, into more complicated forms, and characterized by having two or more contacts imbedded in a single liquid mass—Versluys[1] calls this the funicular stage. Finally there is the stage of complete saturation in which a single mass of liquid, completely filling all pores, extends across the soil body and

[1] J. Versluys, *Die Kapillarität der Boden*, Inst. Mitt. f. Bodenk. 7, 117–140 (1917).

possesses a simple continuous capillary surface as boundary—it is the saturation stage.

It is fundamental to observe that whatever the boundary surfaces of the liquid found in the soil body, they are capillary surfaces possessing definite curvatures and as such are subject to the laws of thermodynamics and capillarity. When the system is in stable thermodynamic equilibrium, the vapor pressures have definite values throughout the soil column. In the experiment just described the vapor pressures at any two points, at an equal distance above the free liquid, are identical. Kelvin's[2] investigations furnish a criterion for determining the curvatures of a stable capillary surface over which a given vapor pressure exists.

Kelvin's theorem enables us, further, to assign definite curvatures to surfaces in equilibrium at a given distance above a free liquid. For, according to Kelvin,[2] if two similar masses of liquid, confined by identical boundaries, are at equal distances above a free liquid, and if, further, one is in communication with and the other isolated from the free liquid, then not only the vapor pressures over each, but the respective curvatures of corresponding parts of each surface are equal. We may, for example, consider a single ring of liquid wrapped around the contact point of a pair of grains and isolated from the free liquid, and a similar ring in communication with the free liquid—communication can be accomplished by a pipe, one end of which opens into the free liquid and the other, running through one of the grains, opens into the ring at the contact point; if both rings are at an equal distance h above the free liquid, the vapor pressures are equal and hence the curvatures are also equal. We can, therefore, consider a single isolated liquid mass, for example the single liquid ring, as if it were in communication with a free liquid and determine its equilibrium from the well known curvature relation of Laplace; the curvatures of all capillary surfaces existing in the soil body can be found. We shall, throughout this discussion, suppose complete wetting.

The curvatures of any element of the capillary surface are given by the equation,

$$\Delta p = \sigma(1/R_1 + 1/R_2), \tag{1}$$

where R_1 and R_2 are the principal capillary radii of curvature of the given element, Δp the pressure drop across it and σ the surface tension. If we multiply Eq. (1) by $dS \cos \phi$ and integrate over the whole capillary surface, we find[3]

$$\int \Delta p \, dS \cos \phi = \int \sigma \cos \theta \, ds \tag{2}$$

where dS is an element of area of the meniscus, ϕ the angle which the normal to this element makes with the vertical z-axis, ds an element in the meniscus grain contour and θ the angle between the vertical and that normal to ds which is tangent to the meniscus. We shall apply Eq. (2) to a single ring of liquid, and then calculate the quantity of liquid retained in the pendular region of the soil.

If we suppose complete wetting and apply Eq. (2) to the ring shown in Fig. 2a, we find, neglecting small quantities of the order of a grain radius that

$$\Delta p 2\pi r \sin\theta(2r - 2r\cos\theta) = 2(2\pi r \sin\theta)\sigma\cos\theta,$$

from which

$$\sec\theta = 1 + \sigma/(r\Delta p), \tag{3}$$

r being the grain radius. The angle θ may be taken as a measure of the size of the ring; the angle of the ring is defined as the angle between the axis (line of centers) of the two adjacent grains about which it is formed and the radius vector from one of the grain centers to the outer edge of the ring on that grain, and is easily seen to equal θ. Eq. (3) enables us, once the grain radius r, the surface tension σ and pressure drop Δp are known, to fix definitely the size of the ring. For the purpose of the present problem we may set $\Delta p = \rho g h$, where ρ is the density of the liquid and g the acceleration of gravity; hence, we find

$$\sec\theta = 1 + \sigma/(\rho g h r), \tag{4}$$

for the size of the stable ring at a height h above the free liquid. This equation is applicable so long as the single rings do not overlap and merge.

To find the actual volume of the ring around two grains in contact we shall make the assumption that the section of the capillary surface

[2] W. Thomson, Phil. Mag. [4] **42**, 448 (1871).

[3] See any treatise on capillarity; e.g., Webber and Gans. *Repertorium der Physik.*

made by a plane passing through the axis is the arc of the circle of radius R tangent to both grains, and that the volume is generated by revolving this arc around the axis. We shall let y be the radius of the circle traced by the capillary surface in a plane normal to the axis and midway between the two grain centers (cf. Fig. 2a). The volume v of liquid in the ring is not difficult to find; for example, let w_1 be the volume of the figure of revolution formed by revolving the circular arc of radius R around the axis, and included between two planes normal to the axis and passing respectively through the points, on each grain, of tangency to the generating arc, and let w_2 be the volume of the grain portions included between these planes, then $v=w_1-w_2$. After a simple integration,[4] we find, on setting $\alpha=R/r$ and $k=y/r$,[5]

$$v/(2\pi r^3)=[\alpha/(1+\alpha)][(k+\alpha)^2-\alpha(k+\alpha)\{1-1/(1+\alpha)^2\}^{\frac{1}{2}} -\alpha(k+\alpha)(1+\alpha)\sin^{-1}\{1/(1+\alpha)\}+\alpha^2-\alpha/(1+\alpha)]. \quad (5)$$

From the geometry of the ring shown in Fig. 2a, we have the relation $(1+\alpha)^2=(k+\alpha)^2+1$, which may be used to simplify Eq. (5) to

$$v/(2\pi r^3)=\alpha^2[1-(k+\alpha)\sin^{-1}\{1/(1+\alpha)\}]. \quad (6)$$

We may express k and α in terms of θ; from Fig. 2a we see that

$$(1+\alpha)=\sec\theta; \quad (k+\alpha)=\tan\theta; \quad \sin^{-1}\{1/(1+\alpha)\}=(\pi/2-\theta). \quad (7)$$

Substituting these expressions in Eq. (6) we find as an alternative form:

$$v/(2\pi r^3)=(\sec\theta-1)^2[1-(\pi/2-\theta)\tan\theta]. \quad (8)$$

Comparing Eqs. (4) and (7) we see that

$$\alpha=\sigma/(\rho ghr); \quad k=[2\sigma/(\rho ghr)+(\sigma/\rho ghr)^2]^{\frac{1}{2}}-(\sigma/\rho ghr). \quad (9)$$

If, finally, these values of k and α are substituted in Eq. (6), we find

$$v/(2\pi r^3)=(\sigma/\rho ghr)^2[1-\{2\sigma/\rho ghr+(\sigma/\rho ghr)^2\}^{\frac{1}{2}}\sin^{-1}\{1/(1+\sigma/\rho ghr)\}]. \quad (10)$$

One obtains from Eq. (10) the volume of liquid of density ρ and surface tension σ in the form of a ring around the contact point of two grains each of radius r at a height h above a free liquid, and in stable equilibrium; g is the acceleration of gravity. Eqs. (4) and (8) may also be used to derive Eq. (10). Fig. 3 shows the quantity $v/(2\pi r^3)$ represented as a function of h.

In order to compute the total retention in a soil column included between two planes at distances h_1 and h_2 respectively above a free liquid, it is convenient to have an expression for the average ring volume ($\bar{v}$) for all rings between the two heights h_1 and h_2; ($h_2>h_1$). We require

$$\frac{\bar{v}}{2\pi r^3}=\frac{1}{h_2-h_1}\int_{h_1}^{h_2}\frac{v}{2\pi r^3}\,dh. \quad (11)$$

For this purpose we use Eqs. (4) and (8); we find from Eq. (4):

$$dh=\frac{(-\sigma/\rho gr)(\sec\theta\tan\theta)}{(\sec\theta-1)^2 d\theta}.$$

With this value of dh, we find from Eqs. (8) and (11):

$$\frac{\bar{v}}{2\pi r^3}=\frac{1}{h_2-h_1}\int_{h_1}\frac{-\sigma}{\rho gr}\psi(\theta)d\theta, \quad (12)$$

[4] We find:

$$w_1/2\pi=\{(y+R)^2+R^2\}R\cos\theta-(y+R)R^2(\pi/2-\theta) -R^2(y+R)\sin\theta\cos\theta-(R\cos\theta)^3/3$$

$$w_2/2\pi=(2/3)r^3+r^3(\cos\theta)^3/3-r^3\cos\theta,$$

where $\sin\theta=(R+y)/(r+R)$ and $\cos\theta=r/(r+R)$.

[5] cf. Smith, Foote and Busang, Phys. Rev. **36**, 524–530 (1930).

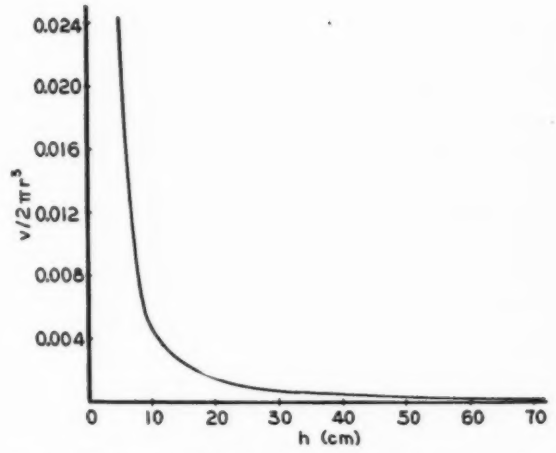

FIG. 3. The quantity $(v/2\pi r^3)$ represented as a function of h for Eq. (10). $\sigma/\rho g r = 1$.

where

$$\psi(\theta) = \{1-(\pi/2-\theta)\tan\theta\}\sec\theta\tan\theta.$$

We set $F(h) = \int \psi(\theta)d\theta$, and obtain[6]

$$F(h) = \tfrac{1}{2}(\sec\theta)\{1-(\pi/2-\theta)\tan\theta\} + \tfrac{1}{2}(\pi/2-\theta)\log\tan x + x\{(\log x)-1\} + (x^3/9)\{1+7x^2/50+62x^4/2205+\cdots\}, \quad (13)$$

where $x = \frac{1}{2}(\pi/2+\theta)$. To find $F(h_1)$ and $F(h_2)$, values of θ_1 and θ_2 are determined by use of Eq. (4) from the corresponding values of h_1 and h_2. We find from Eqs. (12) and (13) that the average volume of the ring in the pendular zone between the planes at distances h_1 and h_2 from a free liquid surface is

$$\frac{\bar{v}}{2\pi r^3} = \frac{(-\sigma/\rho g r)\{F(h_2)-F(h_1)\}}{h_2-h_1}. \quad (14)$$

The limits of the pendular zone must be considered. This zone is confined to the part of the soil column in which single rings of liquid exist; when the single rings begin to merge we pass into the funicular zone. It is not difficult to fix the value of θ at which the rings commence to merge. The soil, here considered, is composed of spherical grains of one size packed at random. The value of θ at which two rings touch and merge is determined by the angle δ between the axes of the two adjacent grain pairs supporting them. These relations are shown in Figs. 4, a, b, c. Obviously this phenomenon will first occur when the axes of the three grain pairs involved form an equilateral triangle; hence $\theta = 30°$. We find from Eq. (4) that, for this value of θ, overlapping commences when $(\rho g h r/\sigma) = 6.452$. Thus $h = 6.452(\sigma/\rho g r)$ fixes the lower limit of the pendular zone; the upper limit is the top of the soil column, including h infinite as the extreme upper limit. Values of $(\rho g h r/\sigma) < 6.452$ down to values of this quantity required for saturation are in the funicular zone.

To find Ω_p the total volume of liquid per cc of packed space, in the pendular zone, it is necessary to know the total number of contacts N per cc (of packed space). For this purpose we suppose the quantity N plotted, as in Fig. 5, as a function of the corresponding porosity P. N_h and N_c are points of this curve, where N_h and N_c are the numbers of contacts per unit volume for close hexagonal $(P = 0.260)$ and cubic $(P = 0.476)$ pilings respectively; $N_h = 6(2^{\frac{1}{2}})/8r^3$ and $N_c = 3/8r^3$, for two grains are required for each contact. We make, as a first approximation, a simple interpolation between these values to find N. From Fig. 5

$$\frac{(N-N_c)}{(0.476-P)} = \frac{(N_h-N_c)}{(0.476-0.260)}.$$

We find

$$N = N_h x + N_c(1-x),$$

where

$$x = (0.476-P)/(0.217), \quad (15)$$

and substituting the values of N_h and N_c given

---

[6] We find

$$\int\psi(\theta)\,d\theta - \tfrac{1}{2}(\sec\theta)\{1-(\pi/2-\theta)\tan\theta\} + \tfrac{1}{2}\int(\pi/2-\theta)\sec\theta\,d\theta.$$

Now

$$\int(\pi/2-\theta)\sec\theta\,d\theta = (\pi/2-\theta)\log\tan\tfrac{1}{2}(\pi/2+\theta) + \int\log\tan\tfrac{1}{2}(\pi/2+\theta)\,d\theta.$$

To find $\int \log\tan\frac{1}{2}(\pi/2+\theta)\,d\theta$ we set $x = \frac{1}{2}(\pi/2+\theta)$ and integrate in series. The series for $\log\tan x$ (cf. B. O. Pierce, *Short Table of Integrals*) is convergent for all values of $x^2 < (\pi/2)^2$; θ is in general 30° or less, as will be shown later; hence $x = \frac{1}{2}(\pi/2+\theta)$ generally has its greatest value near unity, and the integration is within the region of convergence.

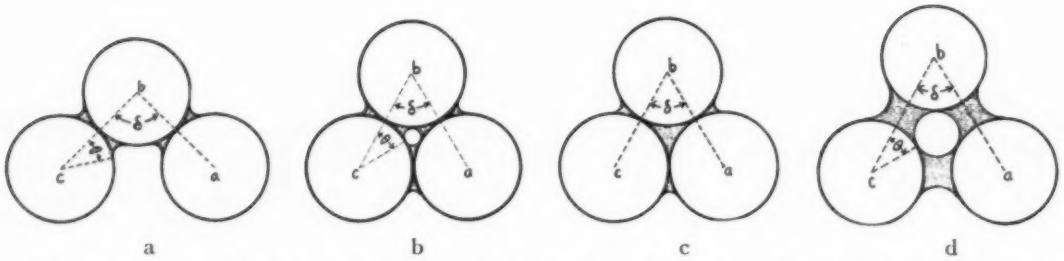

FIG. 4. Transformation of single liquid rings. (a) Single rings with angle $\delta > 60°$. (b) Single rings about to merge in three grain pore with $\delta = 60°$. (c) Simple web of liquid existing after coalescence of rings. (d) Rings of liquid in spaced hexagonal packing, with $\delta = 60°$.

above we find[7]

$$N = 3(1+1.828x)/8r^3. \tag{16}$$

In the pendular zone, finally, the average volume of liquid Ω_p retained per cc of packed space is given by

$$\Omega_p = \bar{v}N, \tag{17}$$

where N is given by Eq. (16) and $\bar{v}$ by Eq. (14). In a volume V of packed space the total retained liquid is $\Omega_p V$ cc.

For the purpose of determining the distribution of liquid in the soil, the quantity retained per cc of packing is required to be known for a lamina of soil at a height h above the free liquid. The variation of v in a small interval is approximately linear and we may, for this purpose, disregard the averaging process. We may set

$$\Omega_p = vN, \tag{18}$$

where v is given by Eq. (10) and N, as before, by

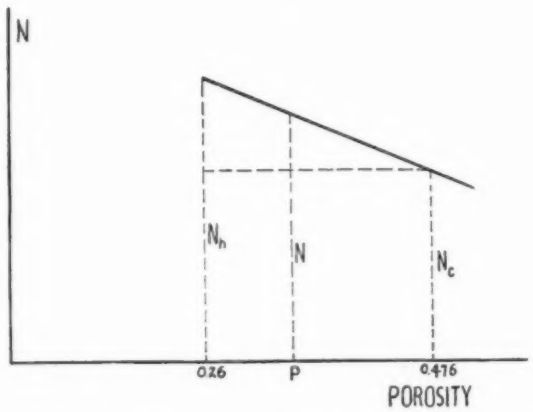

FIG. 5. Number of contacts per cc of packing represented as a function of porosity P.

Eq. (16). The value of v at the center of the lamina under investigation only need be considered; the increased moisture below this point is closely compensated by the decrease in moisture above.

The distribution of liquid in the funicular zone is complicated and presents, throughout, a variability not found in the simpler pendular zone; hysteresis is a commonly observed effect. Not only single rings of liquid but more complicated forms, namely, webs of liquid enmeshing two or more grains, are present. It is possible to have single pores completely saturated or even several associated pores in that state. For example, the random tetrahedron formed by the centers of any four associated grains, not in regular array, may be completely filled; or else, the retained liquid may be confined to masses symmetrical about the faces of the tetrahedron (i.e., the webs of liquid which may extend to adjacent tetrahedrons); or we may have, finally,

[7] It is not difficult to show that the average number of contacts per grain derived from Eq. (16) is identical with the value given in an earlier paper (Smith, Foote and Busang, Phys. Rev. **34**, 1271–1274 (1929)). We note that the number of grains m per unit volume, in a packing of porosity P, is found by a similar interpolation. We find, as above, $m = m_A x + m_c(1-x)$ where m_A and m_c are the number of grains per unit volume for close hexagonal and simple cubic pilings respectively; $m_A = (2^{\frac{1}{2}})/8r^3$ and $m_c = 1/8r^3$. We find

$$m = (1+0.414x)/8r^3.$$

The average number of contacts per grain is given by $n = 2N/m$; hence

$$n = 6(1+1.828x)/(1+0.414x),$$

which is the expression given in the earlier paper and found to agree with experiment.

simple rings about contact points. The manner of drainage is usually the controlling factor. Before discussing these effects further, it is convenient to fix the limits of the funicular zone in which they commonly occur.

The upper limit of the funicular zone is its junction with the pendular zone and, as stated earlier, is given by the value of h for which $(\rho ghr/\sigma)=6.452$.

The lower limit is given by the least value of h at which saturation occurs, that is, the minimum height of capillary rise. Liquid, rising into a soil, would ordinarily come to equilibrium when the meniscus occupies the widest opening available in its pore cells. Condensation of vapor, just ahead of the advancing meniscus, gives rise to funicular masses of liquid which pull the meniscus further into the soil; equilibrium is reached, when the rising liquid is just unable to reach them, at the height of minimum rise.

For the purpose of calculating minimum capillary rise[8] the sand is treated statistically and the soil grains moved so that they are in regular array with grain centers spaced at a distance $(2r+d)$; r is the grain radius and d a spacing constant. The value of $(2r+d)$ is given by

$$(2r+d)^3=4(2^{\frac{1}{2}})r^3/3(1-P). \qquad (19)$$

The funicular masses of liquid are now in the form of single rings of liquid wrapped around the axis of each pair of spaced grains as shown in Fig. 2b. We shall consider a single funicular ring and determine its size; from the particular value of θ required for coalescence we shall determine minimum rise and hence the lower limit of the funicular zone.

If we apply Eq. (2) to the new type of ring we find

$$\Delta p 2\pi r \sin\theta\{(2r+d)-2r\cos\theta\} = 2(2\pi r\sin\theta)\sigma\cos\theta,$$

from which if we set $(2r+d)/2r=q$ we find when $\Delta p=\rho gh$:

$$q\sec\theta=1+\sigma/(\rho ghr). \qquad (20)$$

Eq. (20) gives the size of the "funicular" ring at a height h above the free liquid surface, where θ is its angle defined, as before, for rings in contact. From Eq. (19) we find

$$q=(2r+d)/2r=0.9045/(1-P)^{\frac{1}{3}}. \qquad (21)$$

Two rings of the spaced hexagonal soil will merge when their axes make an angle of 60°, hence θ has a value of 30° (cf. Fig. 4d). From Eqs. (20) and (21) we find with $\theta=30°$ that minimum rise is given by

$$(\rho ghr/\sigma)=1/\{1.044/(1-P)^{\frac{1}{3}}-1\}. \qquad (22)$$

Values of $(\rho ghr/\sigma)$ which lie in the funicular zone are, therefore, such that

$$1/\{1.044/(1-P)^{\frac{1}{3}}-1\}<(\rho ghr/\sigma)<6.452. \qquad (23)$$

The value $(\rho ghr/\sigma)=6.452$ is, for actual ideal soils, close to the value of this quantity at the height of maximum capillary rise.[9]

Whether liquid enters the saturation zone by direct rise or by condensation the final result is the same. When the funicular rings of the hexagonal soil merge, each elementary tetrahedron becomes filled; additional liquid must condense until the meniscus has, in each case, a curvature required by the vapor pressure of minimum capillary rise; or less depending on the position of the tetrahedron with respect to the free liquid. Coalescence of these rings will cause liquid to enter all cell types.[8] Because of the symmetrical nature of the piling the whole soil body will become saturated up to the height where the rings are no longer able to merge. The small distortions required to transform the hexagonal soil into an ideal soil will not alter this behavior to any degree. Hence the least value of $(\rho ghr/\sigma)$ at which saturation sets in, in a soil packed to porosity P is given by Eq. (22). This behavior may be observed experimentally with a few metal spheres, for example BB shot, piled in regular array; if kerosene is added carefully the mechanism of ring coalescence and saturation is easily observed.

The funicular zone, as stated earlier, is a zone of hysteresis; a complex of many completely saturated pores, as will be shown later, represents the maximum amount of liquid retained, while the distribution in funicular form (webs and rings) represents the minimum. Exact analysis of

[8] Smith, Physics **4**, 184–193 (1933).

[9] Cf. Smith, Foote and Busang, Physics **1**, 18–26 (1931).

the region is difficult; for it requires a solution of the packing problem, as well as a calculation of the volume included between the bounding surfaces of the actual funicular liquid masses. For the purposes of this paper, we shall consider the average packing and its distribution as sufficient for approximate calculation of the minimum retention. We shall regard the "funicular" rings of the hexagonal soil as representing, above the minimum height of capillary rise, the normal distribution of liquid in the funicular region of an actual soil; the amount of retained liquid is a minimum.

To find the volume of the ring in the spaced hexagonal packing, we proceed as before, and find expressions for w_1 and w_2 identical with those given in reference 4. We set, as before, $\alpha = R/r$ and $k = y/r$ and find an expression for $v/(2\pi r^3)$ identical with Eq. (5). We set $(2r+d)/2r = q$ and find from the geometry of the ring (cf. Fig. 2b) that

$$(1+\alpha)^2 = (k+\alpha)^2 + q^2.$$

Applying this relation to Eq. (5) we find

$$v/(2\pi r^3) = \alpha^2[q - (k+\alpha)\sin^{-1}\{q/(1+\alpha)\}] - (1/3)(q-1)^2(q+2). \tag{24}$$

From Fig. 2b we see that

$$(1+\alpha) = q\sec\theta; \quad (k+\alpha) = q\tan\theta; \quad \sin^{-1}\{q/(1+\alpha)\} = (\pi/2-\theta). \tag{25}$$

From Eqs. (24) and (25) we find the alternative form,

$$v/(2\pi r^3) = q(q\sec\theta - 1)^2[1 - (\pi/2-\theta)\tan\theta] - (1/3)(q-1)^2(q+2). \tag{26}$$

From Eqs. (20) and (25) we see that

$$\alpha = \sigma/\rho ghr; \quad k = \{2\sigma/\rho ghr + (\sigma/\rho ghr)^2 + 1 - q^2\}^{\frac{1}{2}} - \sigma/\rho ghr \tag{27}$$

and we have finally

$$v/(2\pi r^3) = (\sigma/\rho ghr)^2\{q - [2\sigma/\rho ghr + (\sigma/\rho ghr)^2 + 1 - q^2]^{\frac{1}{2}}\sin^{-1}[q/(1+\sigma/\rho ghr)]\} - (1/3)(q-1)^2(q+2), \tag{28}$$

for the volume of the ring of liquid at a height h above the free liquid in spaced hexagonal packing. q is given in terms of the porosity P by Eq. (21). For $q = 1$, that is close hexagonal packing, Eq. (28) reduces to Eq. (10).

The expression for the average ring volume $\bar{v}$ in the funicular zone can be computed as before; we find

$$\bar{v}/(2\pi r^3) = (-\sigma q^2/\rho gr)\{F(h_2) - F(h_1)\}/(h_2 - h_1) - (1/3)(q-1)^2(q+2), \tag{29}$$

where $F(h)$ is given by Eq. (13). The required values of θ_1 and θ_2 are obtained from the known values of h_1 and h_2 by use of Eq. (20); the value of q required for Eqs. (20) and (29) is determined from the known value of P by use of Eq. (21).

To compute the total retention we must know the number N_f of funicular rings per unit volume. The packing used is an average one and we must therefore consider each pair of adjacent grains to support a ring. Each single grain is surrounded by twelve others; hence there are six funicular rings associated with each grain. The number of grains per cc of packed space is $(1-P)/(4/3)\pi r^3$; hence

$$N_f = 9(1-P)/2\pi r^3. \tag{30}$$

The retention Ω_f per cc of packed space is given by

$$\Omega_f = \bar{v}N_f, \tag{31}$$

where N_f is given by Eq. (30) and $\bar{v}$ by Eq. (29). The total liquid retained in a volume V of the funicular region is $\Omega_f V$.

To calculate the distribution, we proceed as in the case of the pendular region (Eq. (21)) and set

$$\Omega_f = vN_f, \tag{32}$$

where v is given by Eq. (28) and N_f by Eq. (30).

It is not difficult, if we neglect distances of the order of a grain radius, to compute the total quantity of liquid in a saturation zone. The total quantity of liquid contained in a cubic centimeter of soil packing is equal to P cc where P is the porosity; that, in a volume V of packing, is VP.

Our discussion has rested, so far, on the supposition that a free liquid surface exists just under the soil body; the purpose has been to ensure the existence, in the soil under discussion, of all three distribution zones. The effect of varying the position of the free liquid surface with respect to the soil body, the effect of complete removal of such surface and finally hysteresis phenomena remain to be discussed.

The position of the free liquid determines the vapor pressures and curvatures existing in the soil body; secondarily it determines the types of distribution zones present. The free liquid surface may be so far below the bottom of the soil column that only the pendular distribution of single rings exists; as it moves closer to the bottom of the soil, it reaches a position that permits pendular and funicular but no saturation zones to exist; and finally it becomes sufficiently close, so that all three zones, as discussed previously, exist. The length of the soil column is of importance; it may be so short that it contains only a funicular or saturation zone depending, of course, on the relative position of the free liquid.

There may be no free liquid surface present at all; the system is supposed closed and contains only the liquid and its vapor distributed throughout the soil body. We suppose equilibrium exists between the liquid and its vapor. To find the distribution of liquid it is necessary to know the vapor pressure distribution in the column. This is fixed, however, if we know the value of the vapor pressure at one point of the column. We shall discuss the problem for two positions of the reference vapor pressure; first, when it is known just beneath the soil column; second, when it is known just above the soil column.

If p is the value of the vapor pressure at any point A, either interior or exterior, of the column, including the reference points selected above, we note it is possible to place a free liquid surface at some distance h_0 below the given point A without disturbing the vapor pressure p already existing at A. The two systems, soil column and free liquid surface, can be united so that the equilibrium of the column is not disturbed. The distance h_0 is chosen so that the value of the vapor pressure at a distance h_0 above the free liquid surface is p. This device permits us to adapt the previous equations without much difficulty.

We suppose, first, the vapor pressure p_B at a point B, just beneath the soil column, is known. The vapor pressure p_0 just above the free liquid surface placed at a distance h_0 below, is known (p_0 depends only on the temperature). We let h' be the distance from B to the given liquid mass, for example, a pendular ring. The height h of this mass above the free liquid surface is $h = h' + h_0$. To apply Eqs. (4) to (32) we need only to use this new value of h. We replace $\sigma/\rho ghr$ by $\sigma/\rho g(h'+h_0)r$. There is a pendular distribution, for example, when $\rho g(h'+h_0)r/\sigma > 6.452$; saturation when $\rho g(h'+h_0)r/\sigma < 1/\{1.044(1-P)^{\frac{1}{3}}-1\}$; and funicular distribution for intermediate values. We can, to a good approximation, calculate h_0. We let D_B and D_0 be the densities of the vapor at the point B and at the free liquid surface, respectively. The height

$$h_0 = \int_{p_B}^{p_0} dp/(gD_B);$$

we assume Boyle's law and find $D_B = D_0(p_B/p_0)$; hence

$$h_0 = (p_0/D_0 g)\ \log_e\ (p_0/p_B). \tag{33}$$

The value of h to be used in finding $\sigma/\rho ghr$ or its reciprocal, for the case of a vapor pressure known at the bottom of the column, is then

$$h = h' + h_0 = h' + (p_0/D_0 g)\ \log_e\ (p_0/p_B). \tag{34}$$

Secondly, we suppose that the vapor pressure p_T to be known at a point T at the top of the column; we let h'' be the distance down to the liquid mass under consideration, and h_0 the distance of the reference point T from the free liquid surface. We have

$$h = h_0 - h'' = (p_0/D_0 g)\ \log_e\ (p_0/p_T) - h'', \tag{35}$$

to be used in calculating $\sigma/\rho ghr$ for Eqs. (4) to (32). The limits of the three distributions can be determined as before. We are thus enabled to compute the distribution of liquid in the closed soil column, provided we know the vapor pressure at a single point, exterior to the column. And likewise if we know the vapor pressure at an interior point; the analysis is similar to that just given.

The distribution above any meniscus of capillary rise must be discussed, for elsewhere[9] the height of rise has been shown to be variable depending on how it is produced. If liquid reaches equilibrium by falling, the height of rise is a maximum. The value of $\rho ghr/\sigma$ just over the capillary surface at this height is roughly that for the lower limit of pendular distribution; for the value of this quantity at maximum rise is, for most ideal soils, close to 6.452, the value given earlier for the boundary of pendular distribution.[9] The height of maximum rise is a stable position of the capillary meniscus and will remain so, as long as the free liquid surface associated with it is undisturbed. The distribution of liquid above it is pendular, except perhaps close to the meniscus where it may or may not be funicular depending on the value of $\rho ghr/\sigma$. The height of maximum rise marks the upper limit of saturation; above it the boundary will not sustain a meniscus extending continuously across the pore space. If, on the other hand, liquid is allowed to rise into the soil it comes to equilibrium at a lower height above the free liquid; the distribution above the height of minimum rise is at first funicular and then becomes pendular. Finally the liquid may be forced to an intermediate position; the distribution is, just above this height, generally funicular and, higher up, becomes pendular. It is obvious that the total quantity of liquid retained in the soil is different for these cases. It is greatest when a meniscus is in the position of maximum rise and least when in that of minimum rise; it is assumed, of course, that the position of the free liquid is, in all cases, the same. This is one phase of hysteresis phenomena, namely saturation hysteresis; there are, because of the variable position of the meniscus, several distributions and values of the total retention possible for the same position of the free liquid.

Saturation hysteresis is dependent on the manner of filling or draining the soil, and can be experimentally demonstrated in the U-system of drainage shown in Fig. 1b. In this apparatus the liquid may be allowed either to rise or else fall to equilibrium. Drainage may be performed under a constant value of $\rho ghr/\sigma$ equal to that of maximum capillary rise. The meniscus may be left in the soil or entirely removed; if it is left in the soil the distribution is that above the maximum rise meniscus, if it is removed the distribution is that given for the minimum meniscus. The final distribution is different, although the position of the free liquid is the same in each case. Fig. 6 shows a schematic diagram of the retention cycle.

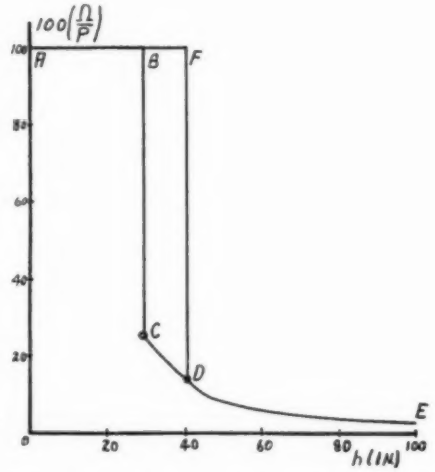

FIG. 6. Schematic diagram of retention cycle: *ABCDE* represents the distribution with the meniscus at minimum capillary rise; *ABFDE* represents the distribution with the meniscus at maximum rise; the area *BCDF* is the region of saturation hysteresis.

With the saturation zone ending at the minimum height of capillary rise, the curve *ABCDE* represents the distribution; it is the normal one and the retention is a minimum. When the saturation zone extends to the maximum height of rise, *ABFDE* represents the distribution. The arc *CD* represents the normal funicular distribution and is computed from Eq. (32); the arc *DE* represents the pendular state and is computed from Eq. (18). The point *B* is fixed by minimum rise and the point *F* by maximum rise. The area *BCDE* defines the region of saturation hysteresis and any point within may be regarded as a stable retention value in the soil. These conclusions are

in agreement with those reached experimentally by Haines.[10]

There is a second type of hysteresis phenomena, a microscopic hysteresis. It is confined to configurations composed of a small number of grains. It is best illustrated by considering a random tetrahedron formed by the centers of four neighboring grains and the possible distribution of liquid within the grains defining it. We suppose the tetrahedron to be in the funicular region. There are, in general, three possibilities. First, we may have simple rings around each actual contact point (the tetrahedron is not supposed to be regular). Second, we consider a single face defined by the centers of three adjacent grains; liquid may be confined within the pore formed by the grains and is bounded by two capillary surfaces, symmetrical about the face, one on the outer side and one facing the interior of the tetrahedron (this is a simple web of liquid). If a single web exists in the tetrahedron, rings may exist at the remaining contacts; a second web, joined to the first may also exist, with the remaining contact occupied by a ring. Finally, the whole tetrahedron may be filled; each face is covered by a capillary surface similar to the outer of the two bounding the single web. In any of these cases the Kelvin equation may be satisfied; the tetrahedron is for each of these forms at the same distance, properly chosen, above the free liquid and each is in equilibrium with the prevailing vapor pressure. The amount of liquid retained is, however, in each case different; when rings exist, it is a minimum and, when the cell is saturated, a maximum. The distribution is thus complicated by the presence of a number of isolated liquid masses each completely saturating the grain configuration supporting it.

There is a definite limit to the size of these liquid forms. As the tetrahedron is farther removed from the free liquid the capillary surfaces bounding the web recede further into the supporting cell, until they meet in its plane of centers. The liquid mass must then break into rings. The extreme case occurs when the cell is saturated; each bounding capillary surface may recede until it occupies the position of a meniscus at maximum capillary rise, the smallest opening of the cell, after which, it breaks into rings. There is, therefore, just as in the case of saturation hysteresis, a definite upper limit to the total quantity of liquid stably retained by the soil when microscopic hysteresis is present. No simple approximation, such as has been used to find the minimum distribution (Eqs. (18) and (32)), however, appears possible.

It is not difficult to fix the limits of microscopic hysteresis. The extreme configuration is a close regular tetrahedron, that is six actual contact points. Each contact point is capable of supporting a ring until these merge when $\rho ghr/\sigma = 6.452$. The tetrahedron may be saturated until the bounding capillary surfaces occupy the smallest opening in each of its faces, that is, the position taken during maximum capillary rise; the height at which this occurs can easily be established. We suppose the tetrahedron saturated and in communication with a free liquid by a pipe running through one of its grains. It is sufficient to consider a single face. We find $\rho gh/\sigma = \pi r/(3^{\frac{1}{2}}r^2 - \pi r^2/2)$; hence $(\rho ghr/\sigma) = 19.5$. The value $(\rho ghr/\sigma) = 19.5$ marks the extreme limit of any hysteresis and is well within the pendular zone. It is obvious that other more open configurations are capable of being saturated as we proceed downward. In an actual ideal soil, the number of close tetrahedrons is not great and becomes smaller as the porosity increases. The normal pendular distribution should not, therefore, be seriously disturbed in the neighborhood of $\rho ghr/\sigma = 19.5$. But as we approach the funicular region, and in this region, larger disturbances are to be expected.

The distribution given by Eqs. (18) and (32), as well as the distribution zones given in this paper are natural ones for absorption. If liquid is allowed to condense from its vapor into a dry soil the amount of retained liquid is a minimum (providing, as is here supposed, surface condensation is negligible) and the distribution is that given by these equations. In the drainage problem, on the other hand, liquid is deposited by the passage of a capillary meniscus through the soil, and the amount of liquid so deposited depends entirely upon the manner of drainage.

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[10] W. B. Haines, J. Agri. Sci. **20**, 97–116 (1930); cf. B. A. Keen, *The Physical Properties of the Soil*, Longmans, Green and Co. (1931), chapter III.

After liquid is placed in the soil by drainage a temporary adjustment quickly takes place. Whatever flow over the grains takes place occurs at this stage; liquid flows to the parts of the grains where it can exist stably, for example, the simple rings of liquid at contact points. All further adjustments are by distillation from some liquid masses and condensation on others; the final state is controlled entirely by the Kelvin equation. It is believed that this latter process is responsible for the slow movement and migration of soil moisture; rather than any flow over the grain surfaces, which according to our view occurs only in the initial stage of moisture adjustment and then only locally. When liquid is placed in a soil by a capillary meniscus moving through it, the microscopic forms are in general fixed and the only further physical process occurring is that of distillation and condensation until the curvatures of the minute capillary surfaces bounding these forms are adjusted to satisfy the Kelvin equation. From what has been said, it is apparent that the soil boundary offers several types of surface satisfying the governing Kelvin equation and just which of these exist in the final distribution depends upon the kind of liquid bodies initially placed in the soil during drainage. These multiple effects are confined, of course, to the hysteresis region. In a straight absorption process, from vapor, such as would take place in an initially dry soil, they do not exist and the normal distribution prevails.

King[11] determined the distribution and total retention of water in a column of uniform sand after it had stood, practically closed, for a considerable interval. His apparatus, shown in Fig. 1c, consisted essentially of a column about 8 feet in length provided with a small capillary C at the top so that atmospheric pressure prevailed. The liquid was allowed to drain into the small bottle D at the bottom, also provided with a capillary E. King filled the column by allowing liquid to enter at the bottom and rise to the top, and then drained it. He allowed the soil with its liquid contents, to stand for a period of approximately $2\frac{1}{2}$ years; drainage into the bottle D was recorded continuously during the interval. He finally measured the distribution and total retention. To determine the distribution, he cut the column into sections 3 inches long, and, by weighing, determined the moisture content of each. His values are recorded as percentages of the total dry weight of sand in the section. Data are given for five different sands, all graded.

There are, however, several objections to the use of King's data for comparison purposes. Unfortunately he does not state the vapor pressures at either the top or bottom of the column. Nor does he state if a free liquid exists below the soil; water collected in the bottle D would serve the latter purpose, but, as to this, he gives no definite information. There is a further objection to his method of filling the column prior to drainage. When liquid is introduced at the bottom, as King has done, large masses of air are trapped in the soil; normally saturated zones will contain, therefore, less than their full quota of liquid for a long period of time. Finally, the grains are far from being spherical.

Figs. 7a to 7e, inclusive, show curves for the data of King and represent, for each of his samples, the percentage of saturation existing in a lamina at the height h above the bottom of the soil. For these curves his data giving the amount of retained liquid as a percentage of the total dry weight of a section have been expressed as percentages of saturation. It appears reasonable, for the purpose of plotting these results, to consider the variation of the liquid quantity to be linear in each section; hence the percentage of saturation for each section is taken to be that at its center. Curves showing the distribution predicted by Eqs. (18) and (32) are also given; these are represented by a full line while a dashed line is used to represent the experimental results of King.

It will be observed that each of the calculated curves of Fig. 7 shows three well-defined regions: a horizontal part AB which represents complete saturation; a steep part CD corresponding to the funicular distribution (Eq. (32)); and finally a flat portion DE for pendular distribution (Eq. (18)). The abscissae of the points B and E are each equal to the height of minimum capillary rise; the point D marks the limit of pendular

[11] F. H. King, 19th Annual Report U. S. G. S., Part II, 59–294 (1897–1898); for the experiment here cited see pp. 85–95.

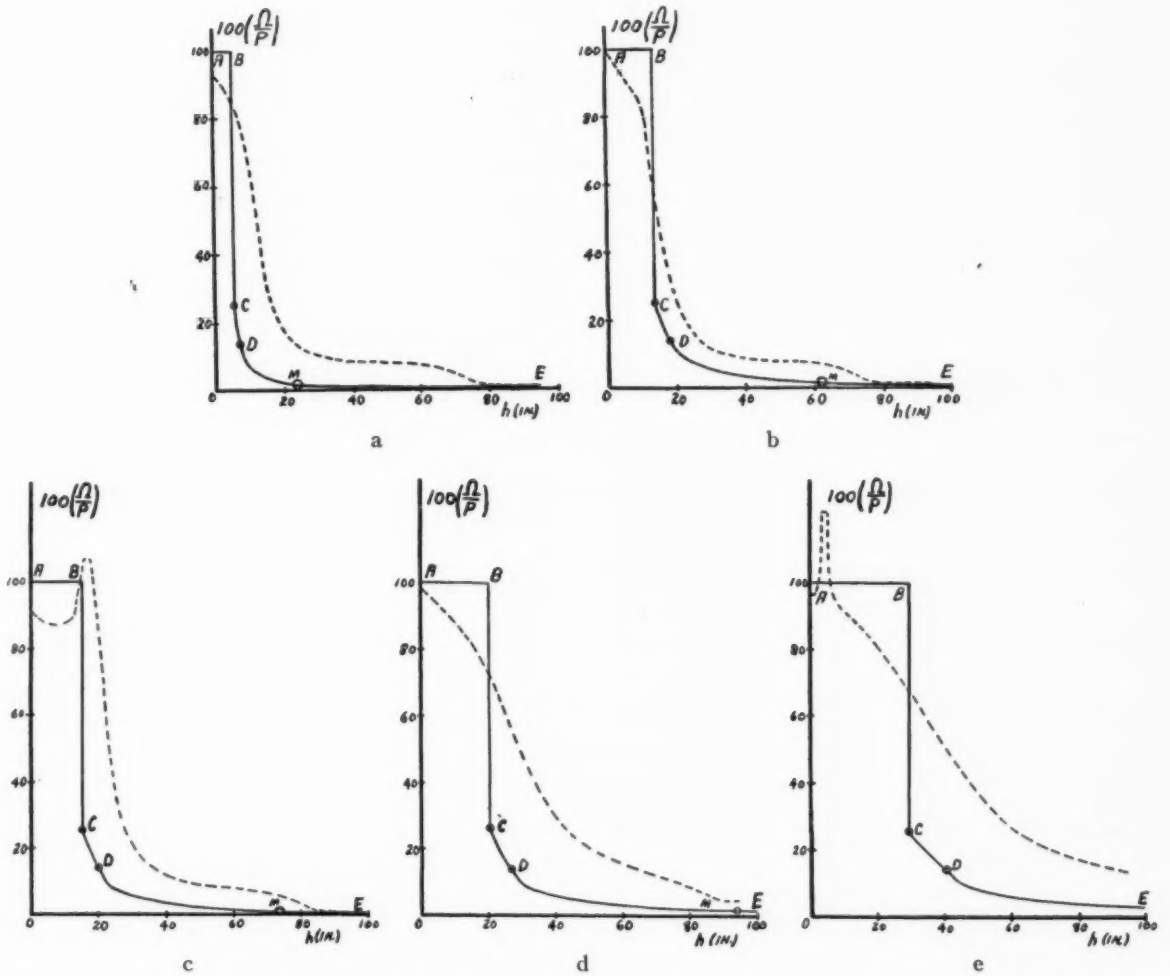

FIG. 7. Distribution of retained water in King's experiments. The full lines represent the distribution calculated from Eqs. (18) and (32); AB is the saturation region; BCD is the funicular; DE is the pendular; m marks the limit of microscopic hysteresis. The dashed lines represent King's data. (a) Sand No. 20; (b) sand No. 40; (c) sand No. 60; (d) sand No. 80; (e) sand No. 100.

distribution. BC is a straight line parallel to the axis of ordinates and extends over the discontinuity between the saturation and funicular regions of the soil. BCD may be considered to define the funicular region of the soil. The same division is suggested, to a greater or less degree, by the experimental curves.

Equilibrium, it should be observed, is established by distillation of vapor from one mass and condensation on a lower one. If the system is closed and contains besides the soil only the liquid and its vapor, it should be established quickly. When, on the other hand, the pores are filled with a mixture of air and vapor, the time to reach equilibrium is lengthened. The early stages of readjustment proceed rapidly, but not so with the later stages; equilibrium depends on the diffusion of vapor through the air in the pore space, and the time to reach the final state may, in packings with small grains and hence very narrow channels, be, therefore, considerable. Comparison of the curves would indicate that the coarser of King's sands are pretty near to equilibrium, while the finer are not. Hysteresis, of course, is in all probability present, and, though the sands were in equilibrium, the experimental curves would still lie above those given by Eqs. (18) and (32).

TABLE I. *Summary of values of zone and total retention for King's experiments.**

Sand number	20	40	60	80	100
Porosity (P)	0.389	0.401	0.408	0.406	0.398
Radius of grains (cm)	0.02373	0.00924	0.00776	0.00592	0.00413
Height of column (cm)	243.9	243.9	243.9	243.9	243.9
Minimum capillary rise (cm)	13.40	33.26	38.80	51.10	74.92
Maximum capillary rise (cm)	18.71	45.55	52.29	69.76	102.9
Limiting height of microscopic hysteresis (cm)	60.4	155.0	184.6	242.0	347.0
Length of saturation zone (cm)	13.40	33.26	38.80	51.10	74.92
Length of funicular zone (cm)	6.56	18.00	22.70	29.10	39.70
Length of pendular zone (cm)	223.9	192.6	182.4	163.7	129.3
(Average vol. of liquid per cc of saturated zone)/(porosity)	1.0	1.0	1.0	1.0	1.0
(Average vol. of liquid per cc of funicular zone)/(porosity	0.200	0.199	0.198	0.191	0.197
(Average vol. of liquid per cc of pendular zone)/(porosity)	0.0109	0.0250	0.0285	0.0301	0.0516
V = Total volume of packing (cc)	30910	30910	30910	30910	30910
V' = Vol. of liquid required to saturate the total pore space (cc)	12030	12400	12610	12550	12300
Vol. of liquid in saturation zone expressed as a percent of vol. V'	5.50	13.60	15.90	21.00	30.70
Vol. of liquid in funicular zone expressed as a percent of V'	0.54	1.47	1.84	2.28	3.21
Vol. of liquid in pendular zone expressed as a percent of V'	1.01	1.97	2.13	2.02	2.74
Total vol. of liquid retained expressed as a percent of V'	7.1	17.0	19.9	25.3	36.7
Calc. vol. of liquid retained = Weight (grams) of liquid retained (density = 1)	854.0	2110.0	2510.0	3158.0	4530.0
Obs. weight (grams) of liquid retained (King)	2121.0	2475.0	3515.0	4576.0	5832.0
Calc. weight (grams) of liquid retained expressed as a percent of dry weight of sand	1.71	4.25	5.09	6.53	9.15
Obs. weight (grams) of liquid retained expressed as a percent of dry weight of sand (King)	4.24	5.05	7.25	9.41	11.82

* Water is the liquid used in these experiments; its density is assumed, in these calculations, to be unity and its surface tension 72 dynes/cm.

Table I shows the retention in each zone together with the total retention, computed by the methods of this paper. The average volume of water per cc of packed space in the pendular zone has been calculated from Eq. (17), and for the funicular zone from Eq. (31). All calculations are made on the basis of a free liquid surface present at the bottom of the soil; the assumption is made that this surface exists in the collecting bottle D. King's values for the total retention are also shown.

The experiments of King, it appears, should be repeated under better controlled conditions. It is advisable to use, for experiments of this kind, carefully graded glass pearls such as those used by Green and Ampt in their work on capillary flow or by Haines.[10] A small sample of packed soil, capable of being weighed on a chemical balance ought to suffice. The container for the sample should be so constructed that the soil pores can be evacuated and then filled with liquid. The system should be placed, during drainage, in communication with the liquid vapor at known vapor pressure and the moisture content determined after equilibrium has taken place. The procedure used by Van Bemmelen, Anderson[12] and others in investigations on absorption by silica gel would be helpful; for example, the device of using mixtures of sulfuric acid and water would be useful in securing definite vapor pressures, although complications might arise since the soil body is initially saturated. It ought, however, to be possible, with a procedure of this kind, definitely to control distribution experiments. Finally microscopic studies of single pore cells with their associated liquid, and made at definitely controlled vapor pressures, are desirable.

[12] J. S. Anderson, Zeits. f. physik. Chemie **88**, 191 (1914); also J. W. McBain, *The Sorption of Gases and Vapors by Solids*, London (1932).

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